ASPECTS OF

METALLOSUPRAMOLECULAR CHEMISTRY

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ABSTRACT

This thesis details the silver(I) coordination chemistry of thirty four alkene-containing ligands. The synthesis of thirty two of these ligands is described of which fifteen are unreported compounds. The ligands were designed to fully explore the potential of the silver(I)-alkene synthon in metallosupramolecular chemistry.

Five series of ligand were designed each exploring a different facet of ligand design. Three series explored different ligand cores which included benzene, naphthalene and single atoms such as carbon, oxygen and nitrogen. Another series explored ligands of higher denticity including tri-, tetra- and hexa-substituted benzenes. The last series investigated ligands with functional groups in addition to olefins, in particular, heterocyclic nitrogens. A metal-centred ligand was created from a bifunctional ligand subunit.

The silver(I)-alkene synthon has been used to create a range of assemblies. Polymeric structures were favoured with a variety of one-dimensional polymers with linear, ladder, helical and necklace type structures. Two-dimensional networks were formed, with some showing porosity. Three-dimensional metallopolymers were formed, including an interpenetrated three-dimensional network. Discrete complexes are commonly of the type Ag_2L_2 but with the occasional formation of Ag_2L.

It is shown that silver(I)-alkene interactions can coexists with other stronger interactions such as silver(I)-nitrogen. The deliberate use of bifunctional ligands allowed the formation of many interesting assemblies including an Ag_3L_2 heterotopic helicate. A Cu(I) complex with copper(I)-alkene interactions was identified.

Techniques used to characterise the ligands and complexes include NMR, mass spectrometry, elemental analysis and X-ray crystallography. The crystal structures of seven organic compounds and forty six complexes are discussed.

Chapter One

Introduction

CHAPTER 1

Introduction

1.1 Metallosupramolecular Chemistry

Historically, chemists have used covalently bonded atoms to construct molecules. Near the end of last century chemists realized that molecules themselves could be used as the individual building blocks, like atoms, to form larger assemblies. This field of chemistry is known as supramolecular chemistry,[1,2] and encompasses the study of the way in which molecules themselves interact through weak intermolecular forces, such as hydrogen bonding, van der Waals forces, π-π stacking and electrostatic interactions. While these interactions are individually weak; when a large number of them are employed, robust structures can be formed. Examples of this can be found in nature, such as DNA, where many weak hydrogen bonding and π-π stacking interactions hold DNA strands together.

Metallosupramolecular chemistry[3,4] is a relatively new concept and is based around the concepts of supramolecular chemistry. It utilizes the interactions between organic molecules (L), which act as ligands, and metal atoms (M). This leads to more robust structures, as the interactions between M and L are generally stronger. However the strength of the interaction depends on the nature of M and L, and it can range from very weak to very strong.[5]

An advantageous feature of this type of chemistry is that it is possible to construct relatively complex molecular architectures in a controlled fashion utilizing the concept of self-assembly. While traditional organic chemistry often involves long multi-step procedures, it is possible, in metallosupramolecular chemistry, to form the desired product in high yield by simply combining the chosen ligand and metal in one single step. By encoding structural information into the ligand and metal, spontaneous self-assembly can occur through molecular recognition. A single product is achieved as the self-assembly process is reversible and allows for corrections which means the most stable product is obtained.

To obtain the desired product the component building blocks must be chosen carefully. The metal building block must be bridging and be able to provide the correct geometry. Shown in Figure 1.1 are some common metal geometries and the angles that they can provide.

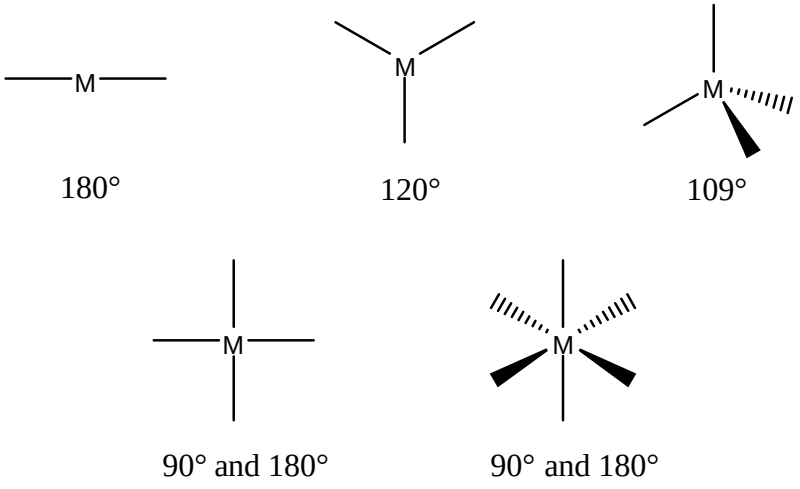


Figure 1.1 *– Some common metal geometries.*

Similarly the component ligand must also be bridging and have donor atoms that are in the correct position relative to each other to provide complementary geometry. Figure 1.2 shows some possible ligand geometries organic molecules can accommodate.

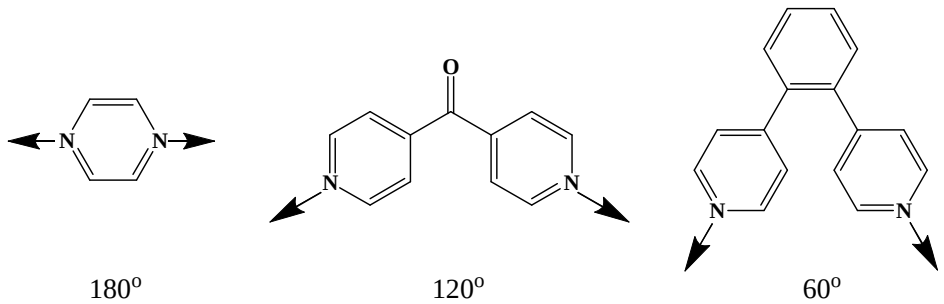


Figure 1.2 *– Geometries available through some bridging organic ligands.*

To construct a simple architecture such as a linear coordination polymer a linear bridging metal and a linear bridging ligand are required. The metal component that will provided

the 180° linkage will typically be two coordinate, the trans coordination of a square-planar ion or the trans coordination of an octahedral ion.

Figure 1.3 *– Schematic of a linear coordination polymer, where the sphere represents a metal ion and the rectangle is the organic ligand.*

Control of the product polymer can arise from ligand design. Using a combination of the same metal component but now using a non-linear ligand it will give rise to a related zig-zag shaped polymer.

This methodology can be extended to make two- and three-dimensional coordination polymers. By using a linear bridging ligand and combining it with different metal components, polymers with higher dimensionality can form. For a two-dimensional polymer, a four coordinate square-planar metal or a doubly capped octahedral metal ion is required, whereas for a three-dimensional polymer a six coordinate octahedral metal is needed.

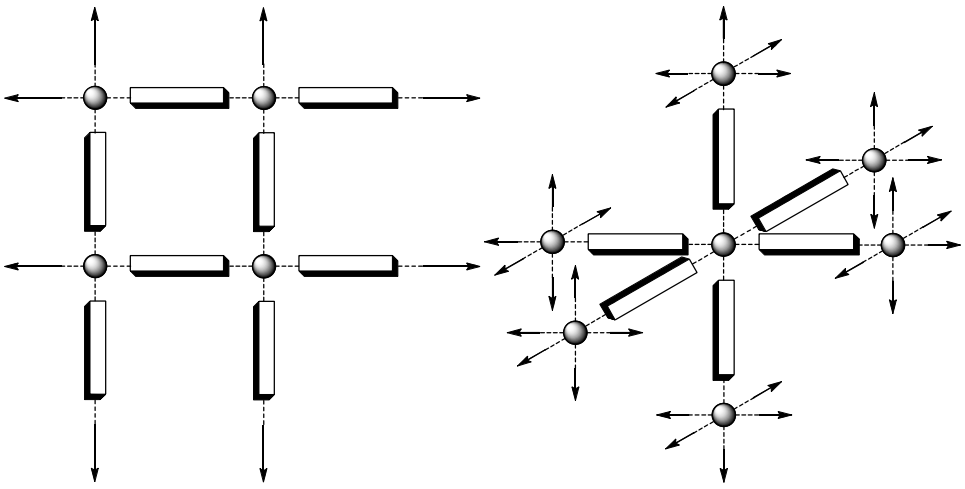


Figure 1.4 *– Schematic of two- and three-dimensional coordination polymers, where the sphere represents a metal ion and the rectangle is the organic ligand.*

Discrete architectures are also accessible through metallosupramolecular chemistry and many interesting two-dimensional polygons and three-dimensional polyhedra can be formed.[6] For example a molecular square can be formed through the combination of four 90 ° angular components and four linear connectors. This methodology can be extended into three dimensions, as in the formation of a cube, by mixing twelve linear components and eight corner units that can connect to three linear components at 90 ° angles. Other metallosupramolecular structures include helicates, rotaxanes, and catenanes.[7-9]

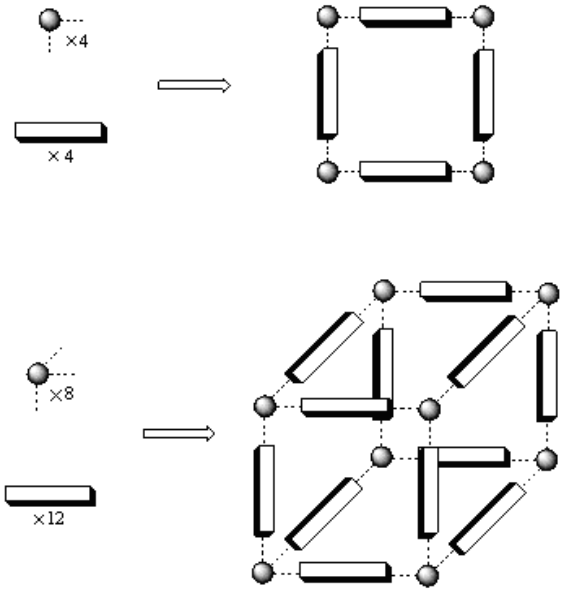


Figure 1.5 *– Requirements for the construction of molecular squares and cubes.*

The size of the desired metallosupramolecular structure can be easily controlled through the rational design of the ligand. By changing from ligand **1.1** to **1.2** the metal-metal separation can be increased from ca 7 Å to 11 Å. Fine control over the metal-metal separation within the assembly can be achieved by using a variety of spacer groups. Figure 1.6 shows various metal-metal separations that can arise from using a combination of just two types of spacer groups.

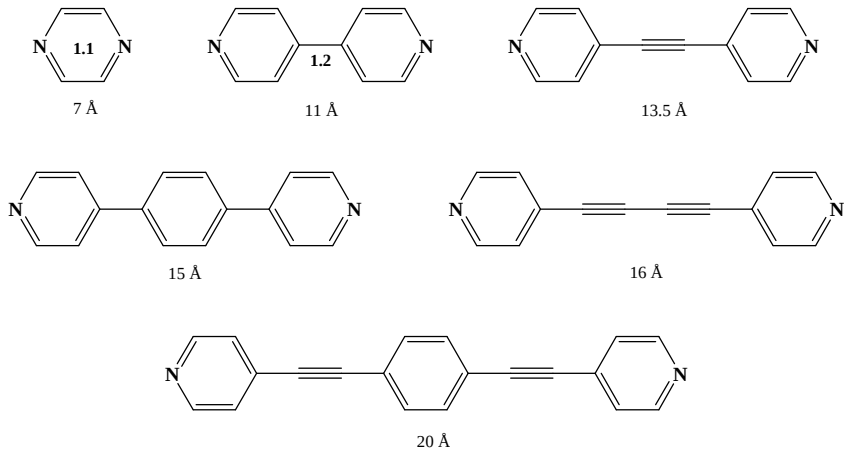


***Figure 1.6** – Linear ligands with differing combinations of spacer groups.*

Ligand **1.1** illustrates the simplicity and versatility of metallosupramolecular chemistry. It gives; a linear polymer when combined with copper(II) perchlorate and 5-chloro-2-hydroxypyridine,[10] a two-dimensional grid when combined with copper(II) perchlorate in a 2:1 ligand to metal ratio,[11,12] a three-dimensional grid when combined with silver(I) hexafluoroantimonate in 3:1 ligand to metal ratio[13] and a molecular square when combined with [(cyclen)$RuCl_2$]Cl in a 1:1 ratio (cyclen = 1,4,7,10-tetraazacyclododecane).[14] For further examples, see review.[15]

Ligands used in metallosupramolecular chemistry can vary greatly in their diversity. However they are confined in that they all must contain functional groups that will coordinate to the chosen metal ion. In most assemblies nitrogen-containing ligands, and in particular nitrogen-containing heterocycles, are used. Nitrogen is used because it forms a relatively strong bond with many transition metals. For example, the nitrogen in pyridine has a lone pair, which it can donate to the metal. As the pyridine π system is electron deficient it can also accept electron density back from the metal, therefore there is partial double bond character[16] thus giving the relatively strong bond between metal ion and ligand.

However potential ligands are not limited to nitrogen as the heteroatom, there are many examples of other heteroatoms, including phosphorus,[17,18] oxygen[19-21] and sulfur.[22] What

this thesis explores is using unsaturated carbon bonds to coordinate to the desired metal ion, which in this case, is silver(I).

1.2 Metal-Alkene Interactions

The first reported instance of a metal-alkene complex was in the early 1800's.[23] The reported complex, shown in Figure 1.7, is a square-planar platinum salt consisting of three coordinated chlorines one coordinated ethylene molecule, with each carbon atom equidistant from platinum, and a potassium counter cation; $K[(C_2H_2)PtCl_3]$. This salt is known as Zeise's salt and is named after the man who first reported it, William Zeise.[23]

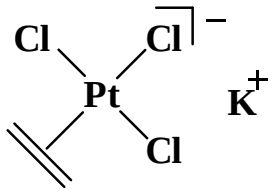


Figure 1.7 *– Zeise's Salt.*

While interest in organometallic chemistry was strong in the early 1900s, unsaturated hydrocarbon complexes were for, the most part, left on the sidelines. It was not until the 1950s that interest increased and an accurate model for the bonding between a transition metal and an alkene was put forth.

Dewar proposed in 1951 that an alkene, or any unsaturated or aromatic hydrocarbon, could form a dative bond with an electron acceptor which includes transition metals. It would occur through the filled π bonding molecular orbitals of the carbon-carbon double bond overlapping with a vacant metal orbital of corresponding symmetry with the potential for backbonding through the overlap of the π^* antibonding orbitals of the double bond and a filled d orbital in the metal which also has the necessary symmetry.[23,24] Additional evidence and slight modification by Chatt and Duncanson[25] lead it to be known as the Dewar-Chatt-Duncanson model.[25]

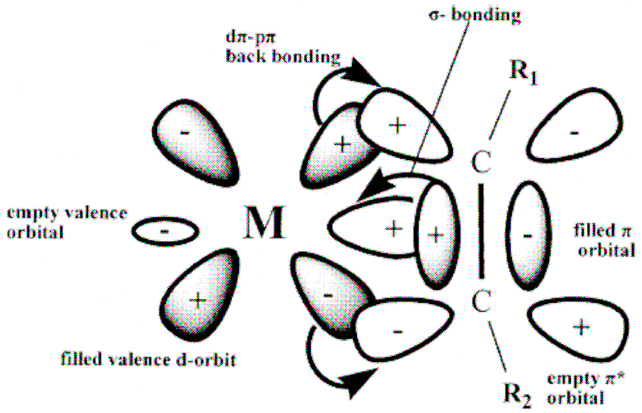


Figure 1.8 *– Orbital description of metal-alkene bonding.*

Computational studies initially done by Ziegler et al.[26] and then in more depth by Hertwig et al.[27] indicate that back-donation plays a more significant role in the bonding between olefins and first row transition metals than it does in the second and third row. Calculated populations, carried out by Bowers et al.,[28] in the 4d-orbitals of Ag^+ remain mostly unchanged when bound to an alkene ligand which indicates minimal back-donation from the 4d-orbitals to the empty π* orbital of the alkene and further confirms that it does not play a large role in the silver-alkene bond interaction. Further information on the calculations can be obtained from the original papers.[26-28] Other groups, through experimental observation, have also concluded that there is no significant π back-donation in the silver(I)-arene* bond interaction.[29-31]

Bowers et al. also established experimental gas-phase bond dissociation energies for $Ag^+(C_2H_4)_n$ and $Ag^+(C_3H_6)_n$ where n = 1 to 6.[28] They found that first two C_3H_6 ligands bind more strongly (39.2 and 32.9 kcal mol^{-1}) than C_2H_4 (32.2 and 30.1 kcal mol^{-1}) and that in both systems there is a significant decrease in the bond dissociation energy (10-20 kcal mol^{-1}) between the second and third ligand. Each additional ligand after this is bound more weakly in both systems. If this should apply to solid state complexes it would be expected that less than four alkenes will coordinate to Ag^+ at any one time.

* Silver(I)-arene interaction denotes an η^2 interaction between a silver(I) atom and an aromatic molecule.

1.3 Silver-Arene Interactions

It has been well documented that silver will not only interact with simple alkenes but will also coordinate to aromatic systems such as benzene.[32-36] Silver(I) can interact with aromatic molecules in an η^1,[37-41] η^2,[39] η^3,[42,43] or η^6 [44-46] manner, although most commonly it will interacted in an η^2 fashion. One of the first complete crystal structures of this type of coordination was published in 1958 detailing a complex of silver(I) perchlorate and benzene which revealed benzene bridging two silver atoms via coordination in an η^2 manner.[35]

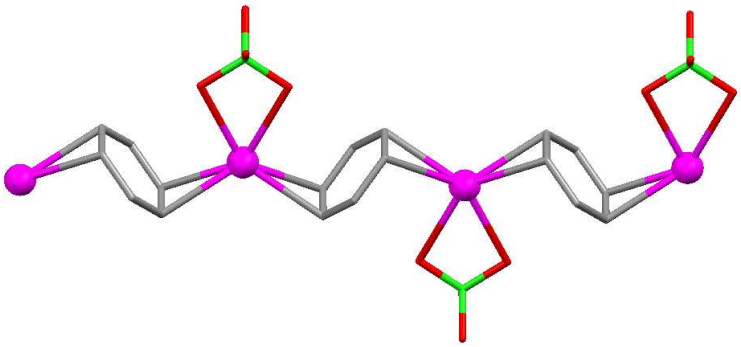


Figure 1.9 *– Silver(I) perchlorate benzene complex determined by neutron diffraction in 1997.*[36]

There are reports that the coordination of silver(I) to an aromatic moiety in an η^2 fashion will lead to the slight elongation of the bond length of the two associated carbon atoms.[36,47] It has been suggested that the lengthening is due to silver(I) reducing the electron density surrounding the two carbon atoms.[47] Conversely, there are reports of the bond length shortening.[35,48] Two possible explanations for this are; that the positive charge on the silver polarizes the π system[35] or that it arises from distortion of the planarity of the aromatic molecule.[48] Other reports have indicated that there is no significant distortion to the aromatic system at all.[34,49]

This type of silver-arene interaction has been exploited extensively in the field of metallosupramolecular chemistry by Munakata et al. This group use polycyclic aromatic compounds as ligands to create multi-layered systems with silver(I). For further

information on this area see the review[50] and subsequent papers[51,52] as well as work done by other groups.[49]

1.4 Silver-Alkene Interactions

Silver(I)-alkene complexes have been known since the 1930s.[53] In the 1950s, 1960s and 1970s there were many simple silver(I)-olefin complexes that were characterised in both solution and solid state by NMR and IR respectively.[54-61] IR clearly indicates the coordination of olefins to silver(I) in the solid state by a shift in the C=C stretching vibration to lower frequencies compared to the uncoordinated olefin.[57] ^{1}H NMR of coordinated olefins will give a characteristic downfield chemical shift compared to the parent olefin the magnitude of which is dependent upon the nature and substitution of the double bond.[57]

There are examples in the literature of silver(I) complexes with the simplest of alkenes, ethylene, which have been characterised in the solid state by X-ray crystallography.[62-66] Silver(I) complexes containing ethylene are rare, as ethylene is easily displaced by weakly donating species and additional supporting ligands, which are generally highly fluorinated and weakly coordinating, are required to stabilise these complexes.

There have been a number of unsaturated hydrocarbons, including natural products, that have been shown to act as ligands to silver(I) and their solid states have been characterised by X-ray crystallography. Such ligands include: norbornadiene (**1.3**),[67-71] 4,7-methano-2,3,8-methenocyclopent[α]indene (**1.4**),[72] trans-cyclooctene (**1.5**),[73] 1,5-cyclooctadiene (**1.6**),[71] 1,5-dimethyl-1,5-cyclooctadiene (**1.7**),[71,74] cyclooctatetraene (**1.8**),[75] *cis*,*cis*,*cis*-1,4,7-cyclononatriene (**1.9**),[76] β-gorgonene (**1.10**),[77] germacratriene (**1.11**)[78] and *cis*,*trans*,*cis*-1,5,9-cyclotridecatriene (**1.12**),[79] pentacyclo[6.6.0.0.0.0]tetradeca-4,11-diene (**1.13**).[80]

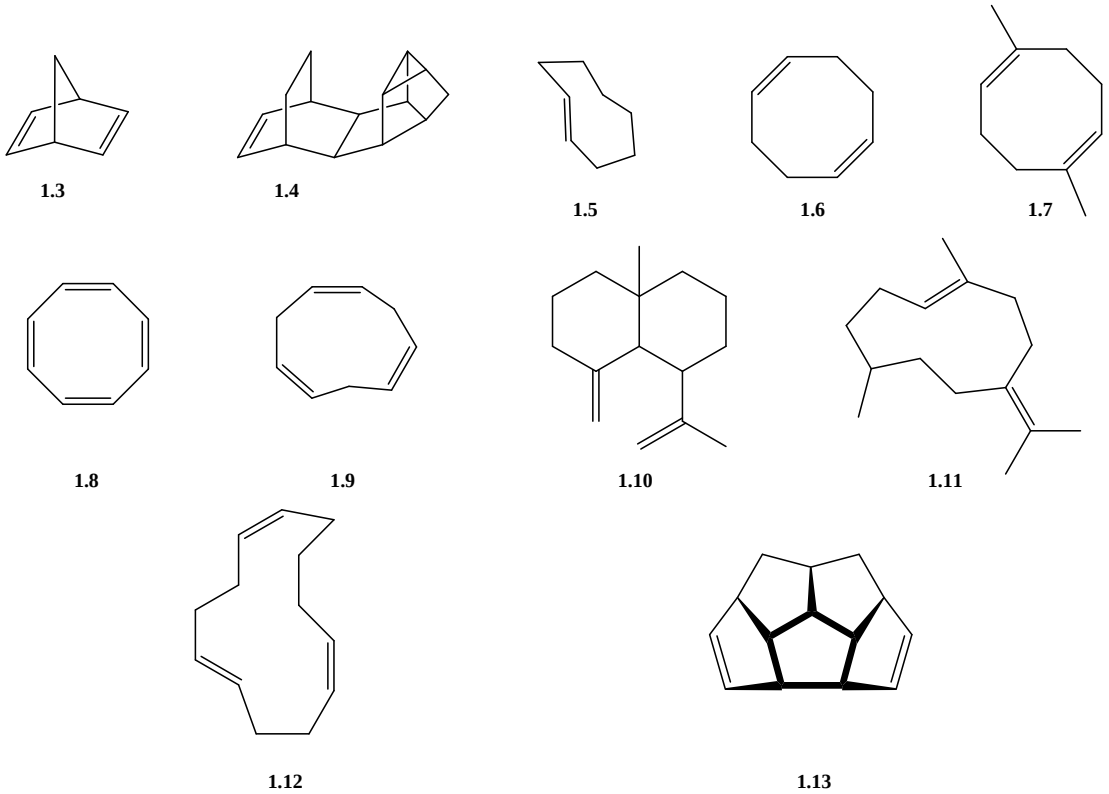


Figure 1.10 *– Unsaturated hydrocarbon ligands that coordinate to silver(I).*

Complexes of ligands **1.3** and **1.8** with silver(I) salts are the earliest examples of these types of systems to be characterised by X-ray crystallography.[67,75] For ligands **1.4**, **1.9**, **1.10**, **1.11**, **1.12** and **1.13**, researchers were exploiting the ability of olefins to coordinate to silver(I) to obtain crystals suitable for X-ray diffraction studies. This in turn enabled the elucidation of the configuration and conformation of the hydrocarbon in question.[76-80] Additionally, previous to the crystallisation of **1.10** with silver nitrate, the silver(I)-alkene interaction was utilised in chromatography to allow the separation of **1.10** from other hydrocarbons.[77] This was also the case for ligand **1.7**.[74]

The use of the silver(I)-alkene interactions for the separation of unsaturated hydrocarbons is an established practice with silver(I) nitrate a commonly used reagent. Methods of separation include impregnating silver(I) nitrate upon solid supports such as silica gel, alumina, amberlyst resin and sephadex, HPLC and precipitating solid silver(I) complexes

with the target compound out of a solution mixture. These methods can be applied to the separation of geometric isomers and constitutional isomers that differ in the placement of olefinic groups, the separation of olefinic containing compounds of different chemical formulae and olefinic impurities from alkanes. For further details see reviews.[81,82]

The silver(I)-alkene interaction is again exploited for its ability to form crystalline complexes to enable X-ray analysis in obtaining rare crystal structures of silver(I) complexes with crown ethers.[83] By incorporating an alkene moiety, shown in Figure 1.11, into crown ethers crystal structure of silver(I) with **1.14** and **1.15** were obtained. The silver is weakly bonded to all four oxygens and the alkene in **1.14** and only three oxygens and more strongly to the alkene in **1.15**.[83]

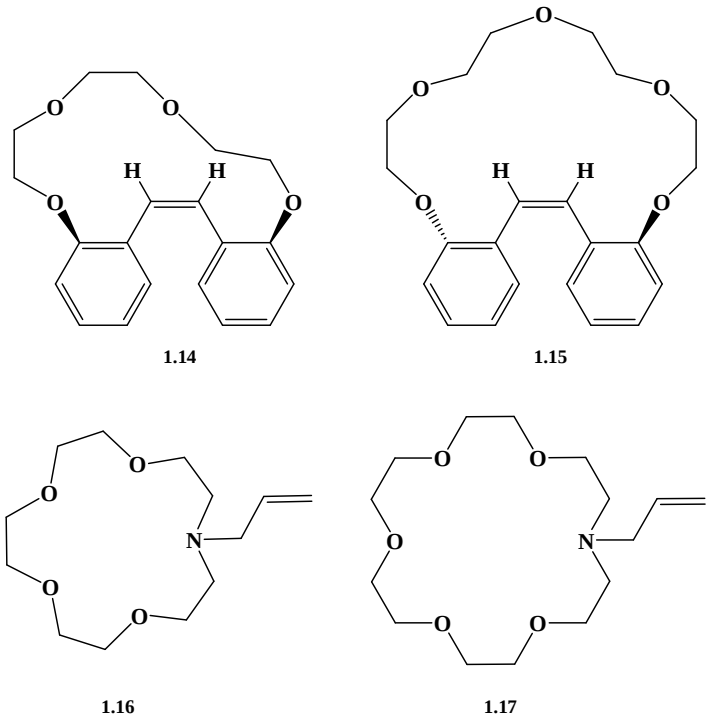


Figure 1.11 *– Modified crown ethers.*

Another modification of crown ethers has been done by Steed, Prince, Cragg et al. where they have attached pendant arms to create allyl lariat ethers such as ligands **1.16** and **1.17** in Figure 1.11. This work is directed at establishing complementary supramolecular hosts for the soft Ag^{+} cation.[84,85] The allyl side arm depending on its length either bridges to a

silver within a second crown ether to form a polymer, or folds back and coordinates to the silver within the same crown ether giving a discrete complex.[85]

Another family of supramolecular host type molecules used to form complexes with silver(I) through the formation of silver(I)-alkene interactions is the annulenes. Three annulenes have demonstrated their ability to form complexes with Ag^+: *all*-Z-tribenzo[12]annulene (**1.18**),[86,87] *all*-Z-tetrabenzo[16]annulene (**1.19**)[88] and pentabenzo[20]annulene (**1.20**).[88]

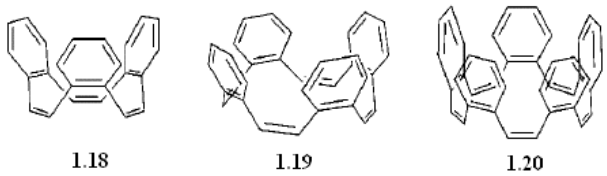


Figure 1.12 *– Annulene ligands.*

Annulene **1.18** has a ridged structure and forms a 1:1 complex with $AgClO_4$. The crystal structure of the complex places the Ag^+ cation at the olefinic end of **1.18**, coordinating to all three alkene moities in the solid state.[86] However the proton NMR suggests that, in solution, there is a possible equilibrium between the Ag^+ located in the olefinic end and in the aromatic cavity.[87] Annulenes **1.19** and **1.20** are more flexible so can change shape to suit the metal complex. Annulene **1.19** gives two different complexes when reacted with silver(I) triflate and perchlorate. Silver(I) triflate gives a one-dimensional polymer with the Ag^+ coordinated to only one olefin, an aromatic ring from an adjacent molecule of **1.19** and the counter anion. Silver(I) perchlorate on the other hand gives a discrete complex with the Ag^+ coordinated to four of the olefins plus the counter anion.[88] The complex formed from the reaction of annulene **1.20** and silver(I) gives a discrete 1:1 complex with the Ag^+ coordinated to four of the olefins with the conformation of **1.20** similar to its free state.[88] What is interesting about these complexes, and is related to this thesis, is that Ag^+ prefers to form silver(I)-alkene interactions over silver(I)-arene interactions.

A relatively new application of silver(I)-alkene interactions is the field of chemical vapour deposition (CVD) of thin films of metallic silver onto surfaces. In general the olefinic groups are in the auxiliary ligands and are used in conjunction with carboxylates or fluorinated diketones.[89-92]

1.5 Silver-Alkene Interactions in Metallosupramolecular Chemistry

The application of silver(I)-alkene interactions in metallosupramolecular chemistry arose when Steel et al. unexpectedly formed a silver(I)-alkene bond in attempts to form molecular triangles.[93] Ligand **1.21** was designed to be the angular component of the triangle and silver(I), in the form of $AgNO_3$, was to be the linear component. The silver not only coordinates to both pyridine nitrogen donors but to the exposed double bond in the bicyclooctadiene unit as well.

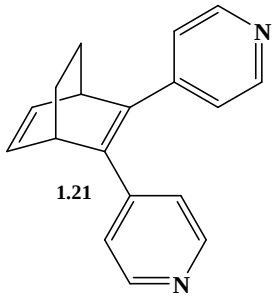


***Figure 1.13** – Angular component, **1.21**, for the construction of molecular triangles.*

Steel et al. concluded that it would be possible to construct metallosupramolecular assemblies using solely silver(I)-alkene interactions. Four natural products, monoterpenes (1S)-(-)-α-pinene (**1.22**) and (1R)-(+)-β-pinene (**1.23**), as well as (R)-(+)-limonene (**1.24**) and γ-terpinene (**1.25**) were used as ligands.[94] Ligands **1.22** and **1.23** only contain one olefinic moiety and were not expected to bridge silver atoms.

The two pinene ligands were reacted in excess with a variety of silver(I) salts and it was found that crystalline adducts formed with **1.22** and $AgClO_4$ as well as **1.23** and $AgPF_6$.

X-Ray analysis revealed both of the resulting complexes to be discrete mononuclear complexes with a ligand to metal ratio of 2:1.[95]

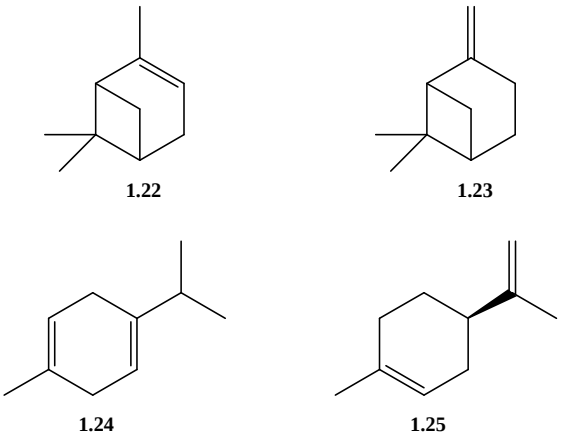


Figure 1.14 *– Natural products used in the field of metallosupramolecular chemistry.*

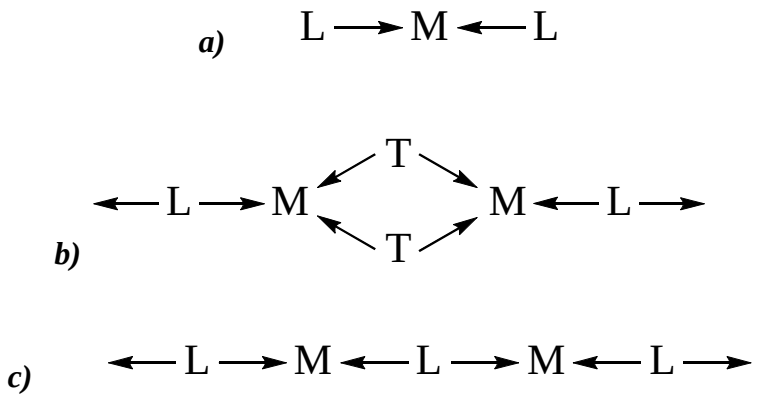
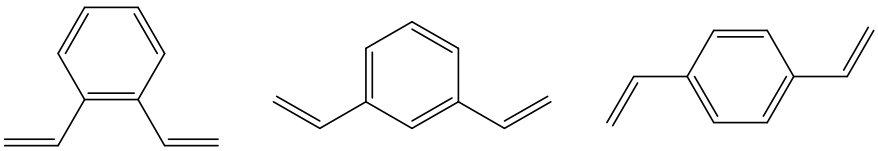


Figure 1.15 *– Schematic drawings of assemblies.* ***a)*** *Discrete mononuclear complexes formed with* Ag^{+} *and* ***1.23***, ***1.23*** *and* ***1.25*** ***b)*** *coordination polymer of* ***1.25*** *and* $AgCF_3SO_3$ ***c)*** *chiral coordination polymer formed with* ***1.24*** *and* $AgPF_6$. *M =* Ag^{+}, *L = organic ligand and T = triflate anion.*

With two olefinic moieties in **1.24** and **1.25** it was expected that they would bridge silver atoms and be capable of forming more complicated assemblies. Ligand **1.25**, although containing two alkenes, (γ-terpinene) still formed a discrete mononuclear complex,

similar to **1.22** and **1.23**, with $AgPF_6$. However upon reaction with $AgCF_3SO_3$ **1.25** bridges silver atoms forming a one-dimensional coordination polymer. Ligand **1.24** also bridges silver atoms and forms a slightly different one-dimensional coordination polymer with $AgPF_6$. (1S)-(-)-α-Pinene, (1R)-(+)-β-pinene and (R)-(+)-limonene are chiral molecules and the chirality is incorporated into their silver(I) complexes.

The repertoire of simple bridging dienes was extended with the exploration of the chemistry of silver(I) with the three isomers of divinylbenzene; *ortho*-(**1.26**), *meta*-(**1.27**) and *para*-(**1.28**).[95] These ligands are slightly different to the previous four in that they now contain an aromatic core which can play a significant role as silver(I) can form silver(I) arene bonds as well.



1.26 **1.27** **1.28**

Figure 1.16 *– Bridging ligands; the three isomers of divinylbenzene.*

Again these ligands were reacted with a variety of silver(I) salts with the formation of crystalline adducts from the reactions of **1.26** with $AgClO_4$, **1.27** with $AgClO_4$, $AgCF_3SO_3$ and $AgBF_4$ and **1.28** with $AgClO_4$. Ligands **1.26**, **1.27** and **1.28** gave coordination polymers with $AgClO_4$ where **1.27** and **1.28** gave one-dimensional coordination polymers and **1.26** a two-dimensional coordination polymer. Additionally ligand **1.27** gave a one-dimensional polymer with $AgCF_3SO_3$ similar in nature to the complex with $AgClO_4$. Ligand **1.26** acted as a tridentate ligand with the third silver atom bonding through a silver(I)-arene interaction. Schematic representations of the coordination polymers are shown in Figure 1.17.

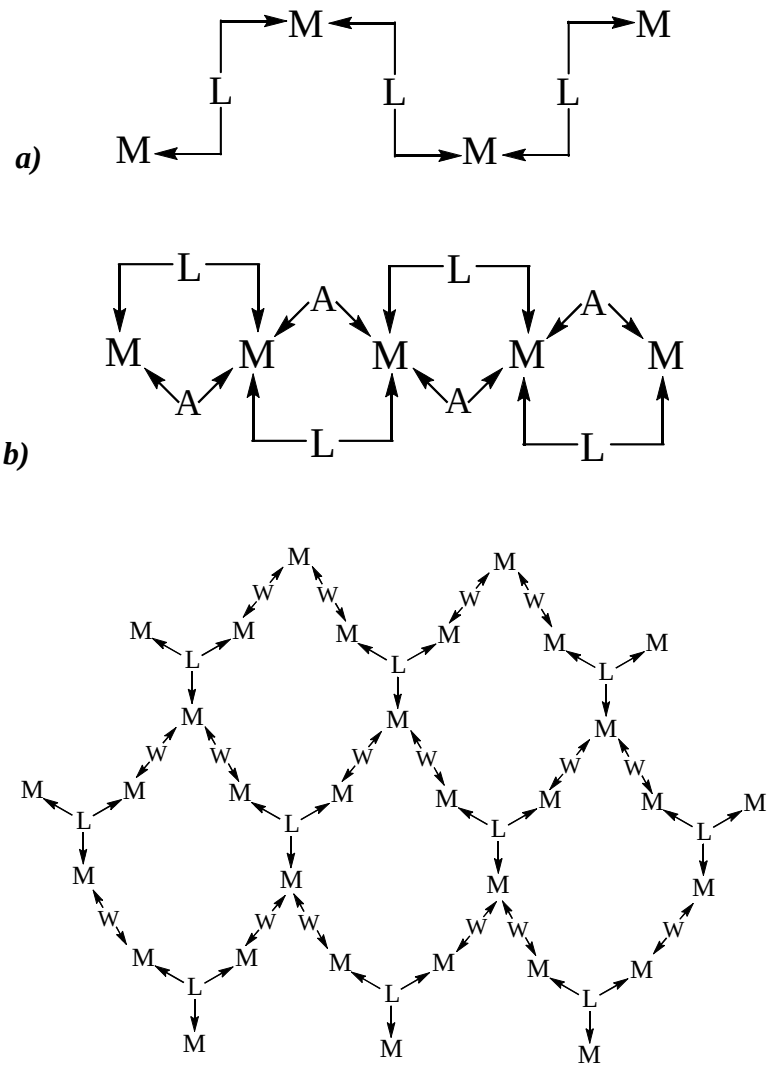


Figure 1.17 *– Schematic drawing of coordination polymers.* ***a)*** *Ligand* ***1.28*** *with* $AgClO_4$ ***b)*** *ligand* ***1.27*** *with* $AgClO_4$ ***c)*** *ligand* ***1.26*** *with* $AgClO_4$ *although the counter anion is coordinating it has been excluded for clarity. M =* Ag^+*, -L- or L = organic ligand, A = counter anion and W = water molecule.*

The reaction between ligands **1.27** and **1.28** with $AgClO_4$ also yielded discrete assemblies. Ligand **1.7** gave a [2+2] macrocycle and **1.27** gave a cage-like structure with a 3:2 silver to ligand ratio. Ligand **1.27** also gave a very similar cage-like structure when reacted with $AgBF_4$. Schematic representations of the [2+2] macrocycle and the cage-like structure are shown in Figure 1.8.

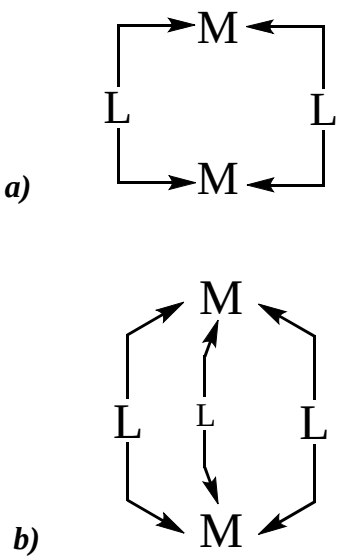


Figure 1.18 *– Schematic drawing of a discrete complexes.* ***a)*** *[2+2] Macrocycle of* ***1.28*** *and* Ag^+ ***b)*** *cage-like structure formed with* ***1.27*** *and* Ag^+ *although the perchlorate anion is coordinating it has been excluded for clarity. M = metal and -L- = ligand.*

1.6 Thesis Coverage

This project expands on the success achieved with simple diene ligands, such as the divinylbenzenes. Many different ligand features, such as the core, flexibility, denticity and functionality are interchanged and explored. A total of thirty nine silver(I)-olefin complexes were isolated and characterised. These complexes have a range of structures from simple discrete units up to three-dimensional coordination polymers. This thesis successfully demonstrates the suitability of the silver(I)-alkene interaction as a basis for metallosupramolecular assemblies.

Characterisation of the ligands was undertaken by ^{1}H NMR, ^{13}C NMR, Mass spectrometry, elemental analysis and X-ray crystallography when applicable. Characterisation of the complexes relied on X-ray crystallography and in some instances ^{1}H NMR.

Chapter two focuses on the addition of spacers units between the benzene core and the olefinic groups in disubstituted benzene ligands. Simple one and two atom additions are employed giving more flexible ligands with each additional atom spacer. Similarities, as well as differences, are seen in the resulting silver(I) complexes.

Chapter three explores the effect of using a larger aromatic ligand core. Ligands that are based around a disubstituted naphthalene core with allyl ether arms as the functional moiety will be used. The combination of a larger aromatic core, olefinic groups and the presence of ether oxygen atoms enables the evaluation of the order of preference for silver(I) to bond to each donor.

Chapter four concentrates on ligands of higher denticity. Ligands are based around a benzene core with vinyl, allyl and allyl ether arms in a 1,3,5-, 1,2,4,5- or hexa-substituted arrangement. The coordination chemistry of these ligands with silver(I) will be explored and discussed.

Chapter five looks at complexes obtained from non-aromatic ligands. Two-, three-, four- and six-armed ligands based around single atom cores will be employed. Their reactions with a variety of silver(I) salts are explored and their resulting complexes will be discussed.

Chapter six explores the silver(I) coordination chemistry with ligands incorporating different functional groups. Each ligand contains an olefinic group as well as either a heterocyclic nitrogen provided by a pyridine core, or a carbonyl oxygen from a pyridone core. Attempts at constructing mixed-metal complexes are also detailed.

Chapter Two

Two Armed Ligands with Benzene Cores

CHAPTER 2

Two Armed Ligands with Benzene Cores

2.1 Introduction

Previous results[95] have shown that simple bridging ligands, such as divinylbenzene, can be used in conjunction with silver(I) to form metallosupramolecular structures. Different structures arose from different substitution patterns of the vinyl groups around the benzene ring. *Para*-divinylbenzene yielded both a [2+2] macrocycle and a zigzag one-dimensional coordination polymer. The *meta* isomer gave one-dimensional metallopolymers and a M_2L_3 cage-like structure, while the *ortho* isomer gave a two-dimensional coordination polymer.[95] This chapter explores the effect of adding spacer atoms between the olefinic function and the benzene ring in simple disubstituted benzene molecules.

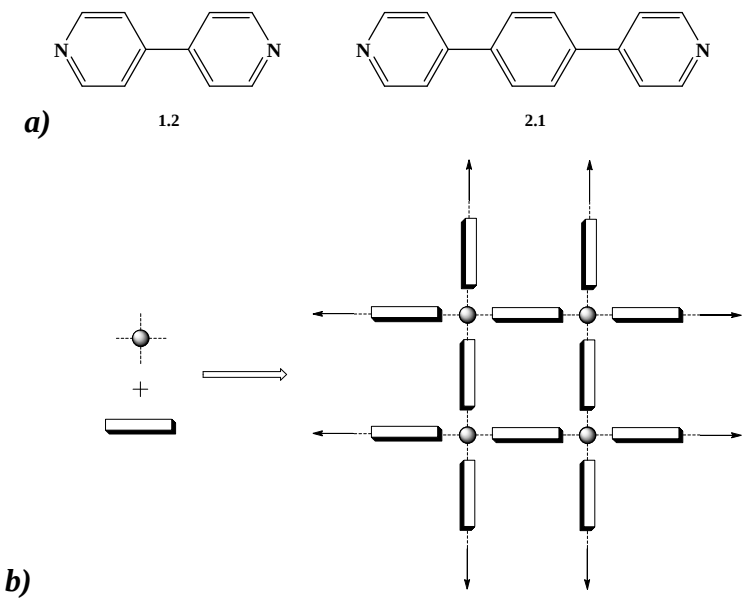


Figure 2.1 – a) *Two linear ligands of differing lengths* ***b)*** *topology of the assembly resulting from the combination of either ligand* ***1.2*** *or* ***2.1*** *with a square-planar four connecting node.*

The addition of ridged spacer groups often results in a product of the same topology but with larger dimensions. For example, when combined with $Cd(NO_3)_2$ in a 1:1 ratio ligand **1.2** forms a two-dimensional square grid. Within the assembly the Cd^{2+} acts as the square-planar four connecting node and ligand **1.2** acts as the linear bridging unit. The squares within the grid have a dimension of *ca.* 11 × 11 Å.[96] Similarly, when ligand **2.1** is reacted with $Ni(NO_3)_2$ in a 1:1 ratio a two-dimensional square grid is also formed.[97] Ligand **2.1**, as with **1.2**, acts as the linear bridging unit and the Ni^{2+} ions act as the square-planar four connecting nodes. While these two ligands form the same topology, ligand **2.1** has an additional benzene spacer group and the dimensions of the squares are bigger with dimensions of *ca.* 15 × 15 Å.[97]

The addition of flexible spacer groups, however, does not guarantee that the products will have the same topology. With the additional flexibility the ligand may be able to interact with the metal ion in new and unexpected ways. Two unsymmetrical ligands, **2.2** and **2.3**, which differ in only one carbon spacer atom highlights this effect. Ligand **2.2** gives a neutral dinuclear copper(II) double stranded helicate when reacted with $CuCl_2.2H_2O$. The two heterotopic ligands are orientated in a head-to-head manner.[98] Alternatively ligand **2.3** gives, under the same reaction conditions, not a $Cu_2(L)_2$ but a neutral $Cu_4(\mathbf{2.3})_4$ assembly which has a slightly distorted tetrahedral geometry. Each copper now has both of the different ends of ligand **2.3** bound.[98]

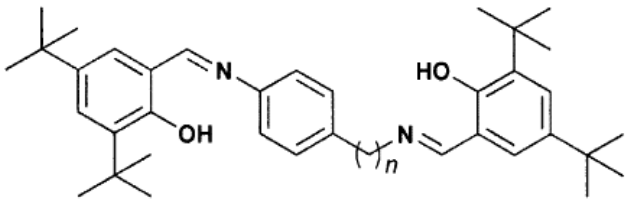


***Figure 2.2** – Two unsymmetrical ligands **2.2**, n = 1 and **2.3**, n = 2.*[98]

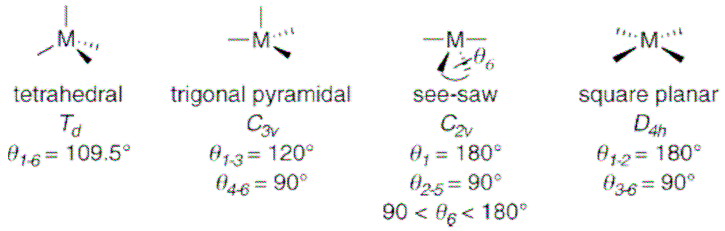
A range between 2.16 Å and 2.94 Å for Ag-C bond distances within a silver(I)-alkene or silver(I)-arene interaction has been reported in the literature.[50,99] In this chapter and

throughout this thesis a silver–alkene interaction is considered to be bonding if the distance is 2.55 Å or less between the silver atom and the centroid of the olefinic carbons. Additionally, both carbons must individually be within 2.65 Å of the silver atom. These distances are somewhat arbitrary and were chosen as they encompass the vast majority of Ag-C distances within this work. This definition also applies to the η^2 coordination of aromatic systems. In the case of η^1 coordination the distance must be 2.65 Å or less between the silver atom and the carbon atom. The sum of the ionic radii between silver(I) and oxygen is 2.66 Å[99] and within this thesis, silver-oxygen interactions are considered bonding when the distance between silver and oxygen is 2.60 Å or less.

The silver-alkene bond is considered a two electron, three centred bond where two olefinic carbons are considered to occupy one coordination site of the silver. The angle between a coordinated olefin and the other coordinated species is calculated from the centroid of the two olefinic carbons. In most of these systems, the geometry about the silver atom is not exact and for four coordinate complexes the parameter τ_4, introduced by Houser et al.[100] is applied. The τ_4 parameter is easily calculated using equation (1) and involves the sum of the two largest angles in the four coordinate species, α and β, subtracted from 360 °, which is then divided by 141 °.

$$\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ} \qquad (1)$$

The values of τ_4 range from 1.00 for a perfect tetrahedral geometry to 0 for perfect square-planar geometry. The intermediate τ_4 values and their corresponding geometries are shown in Figure 2.3. For further information see Houser's paper.[100]



	τ_4
Tetrahedral (T_d)	1.00
Trigonal pyramidal (C_{3v})	0.85
Seesaw (C_{2v}, $\theta_6 = 90°$)	0.64
Seesaw (C_{2v}, $\theta_6 = 109.5°$)	0.50
Seesaw (C_{2v}, $\theta_6 = 154.4°$)	0.18
Seesaw (C_{2v}, $\theta_6 = 170°$)	0.07
Square planar (D_{4h})	0.00

Figure 2.3 *– Geometries and corresponding τ_4 values for four coordinate species.*[100]

There is much debate as to whether silver forms metal-metal bonds. Within metallic silver the Ag-Ag bond length is 2.884 Å[101] and the sum of two silver van der Waal radii is 3.44 Å.[101] Dance et al.[102] report a short Ag···Ag distance of 2.886(4) Å which they described as non-bonding. It was argued that the Ag^+ bonding was fulfilled by two linearly coordinated thiolate ligands and the slight distortion from linearity was indicative of weak repulsion not attraction. However in the light of new theoretical and experimental evidence[103,104] it has been argued that there is indeed significant Ag-Ag bonding.[105]

Two series of disubstituted benzene isomers are used in this chapter, *ortho*- (**2.4**), *meta*- (**2.5**) and *para*-diallylbenzene (**2.6**), as well as *ortho*- (**2.7**), *meta*- (**2.8**) and *para*-di(allyloxy)benzene (**2.9**). *Para*-divinylbenzene, **1.28**, was also used to reproduce results from earlier work.[95] Ligand **1.27** gave different topologies with different counter anions[95] and so all ligands in this chapter and through this thesis are reacted with various silver(I) salts, most commonly silver(I) perchlorate, silver(I) triflate and silver(I) hexafluorophosphate.

The characterisation of silver(I)-olefin complexes in this thesis relies heavily on X-ray crystallography which gives information about the complexes in the solid state. As briefly mentioned in chapter one, silver(I)-olefin complexes can be identified in solution by ^{1}H NMR. Studies were carried out in the late 1960's and early 70's that investigated silver(I)-olefin complexes in organic media by ^{1}H NMR. In particular, one study by Solodar et al.[106] investigated three complexes of $AgBF_4$ with the monoolefins norbornene, cyclohexene and 1-methylcyclohexene in organic solution with NMR. It was revealed that the ligands are very labile and dissociate in solution; as a consequence of this the resulting spectra were of time-averaged equilibria between the complex and the free olefin and silver(I) salt.

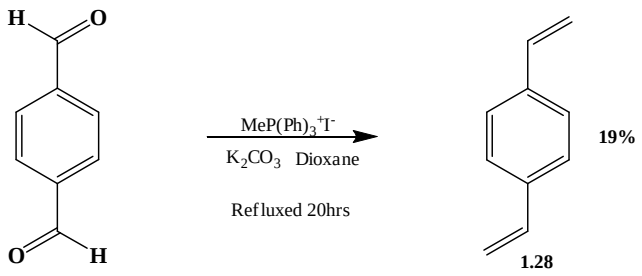
$$[\text{Ag.olefin}]^{+} \rightleftharpoons \text{Ag}^{+} + \text{olefin} \quad (1)$$

Association constants can be calculated for the equilibrium (1) with the resulting K largely dependent on the ligand.[106]

Attempts to obtain spectra that contained the shifts for both the free and coordinated olefin used cooling but no success was achieved down to -55°C. The association constants of the $AgBF_4$ complexes with cyclohexene were calculated in a variety of solvents and it was found the K values were highly dependent on the solvent. In general the more nonpolar solvents gave higher K values. A sample of three complexes; ligand **2.7** with silver(I) perchlorate, silver(I) triflate and silver(I) hexafluorophosphate, have been selected for study in solution by ^{1}H NMR.

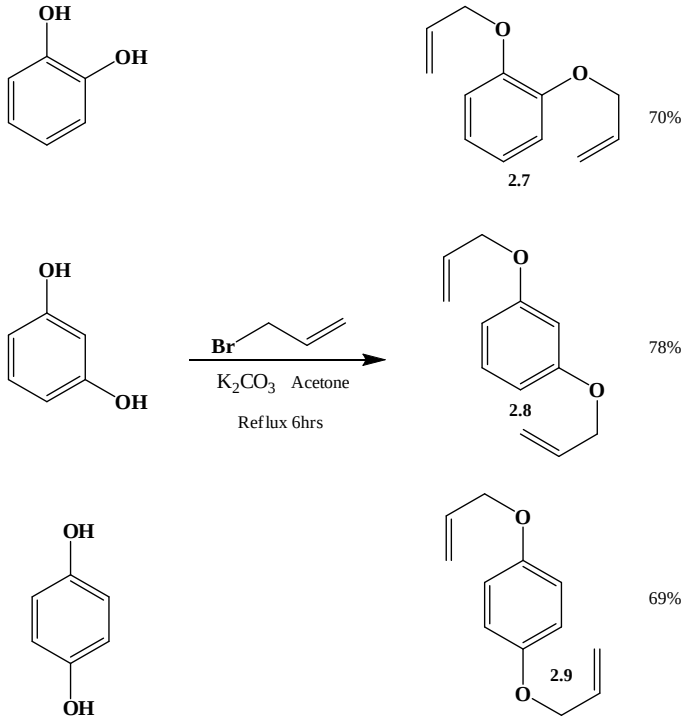
2.2 Ligand Syntheses

The syntheses of the ligands in this chapter utilises simple precursors and established synthetic methods. Ligand **1.28** was synthesised through a Wittig reaction between terephathalic aldehyde and methyl-triphenylphosphonium iodide, shown in Scheme 2.1, resulting in modest yields.



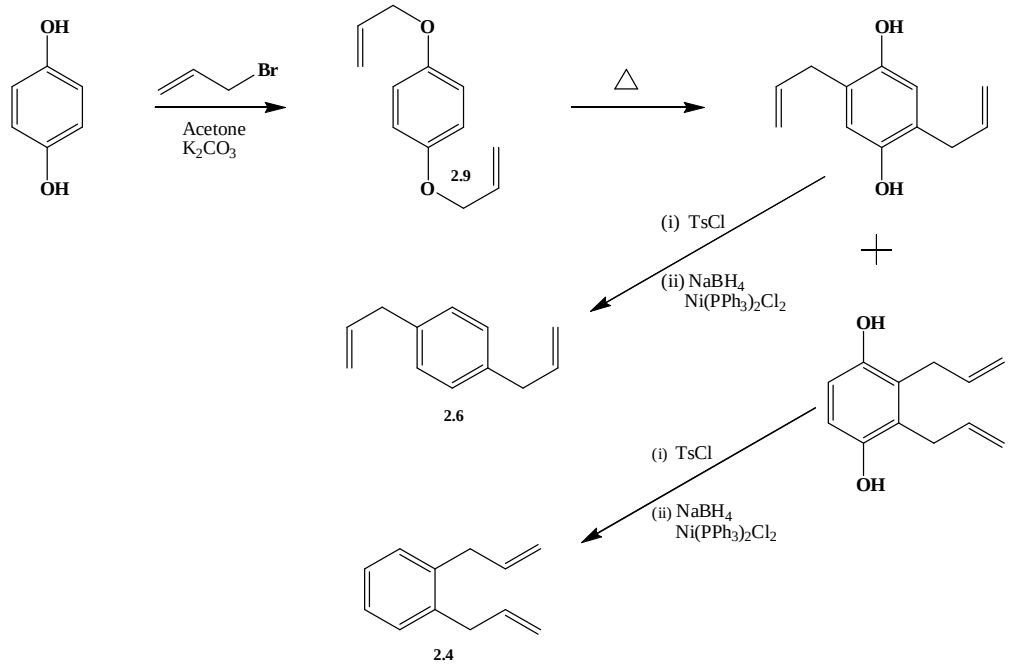
Scheme 2.1 *– Synthetic procedure for ligand* ***1.28****.*

All three isomers of di(allyloxy)benzene are known compounds and a literature procedure[107] was adopted. The procedure utilised a double nucleophilic substitution of the bromine in allyl bromide by the deprotonated dihydroxybenzenes. The method consists of dissolving the appropriate dihydroxybenzene precursor in acetone as well as two equivalents of allyl bromide and potassium carbonate and refluxing the mixture for six hours. This method was used to synthesise all three isomers and gave good yields.



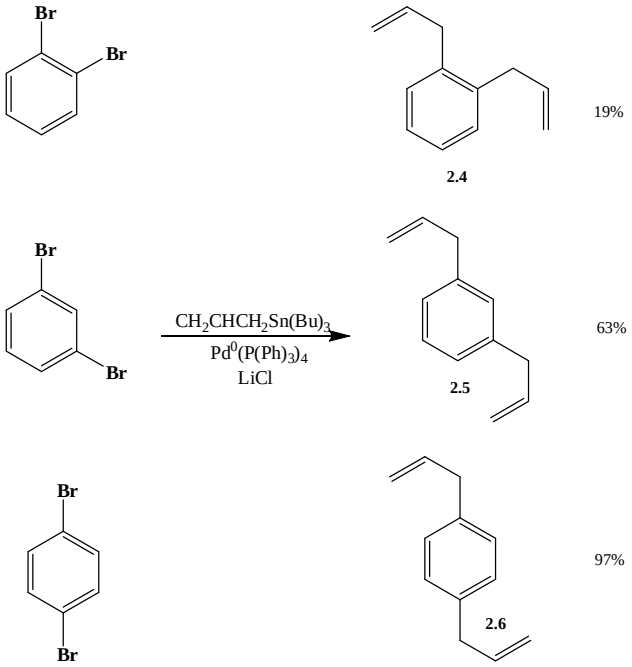
Scheme 2.2 *- Synthetic procedure for ligands* ***2.7****,* ***2.8*** *and* ***2.9****.*

Initially a four step synthesis, shown in Scheme 2.3, was utilised to synthesise *ortho*- and *para*-diallylbenzene. It involved the allylation of a dihydroxybenzene precursor followed by a Claisen rearrangement. This was followed by a double triflation on the rearranged product and then the reductive elimination of the triflate groups to give the desired diallylbenzene.



Scheme 2.3 *– Attempted syntheses for ligands* ***2.4*** *and* ***2.6****.*

Many problems occurred with this procedure particularly in the purification of the rearrangement products. A second much simpler approach was taken which used Stille coupling chemistry cutting the synthetic procedure from four steps to one. The methodology was adapted from a vinylation reaction which used vinyltributylstannane to give trivinylbenzene from the tribromobenzene precursor.[108] To give diallylbenzene, dibromobenzene precursors were heated to 100 °C and were reacted with just over two equivalents of allyltributylstannane in the presence of tetrakis-(triphenylphosphine)palladium(0). The reaction times needed were much greater in the allylation reaction than in the vinylation reaction.



Scheme 2.4 *– Syntheses of ligands* ***2.4****,* ***2.5*** *and* ***2.6****.*

2.3 Complexes of 1,4-Divinylbenzene

With silver(I) perchlorate (**2.10**)

A silver(I)-divinylbenzene complex has already been identified,[95] shown in Figure 2.4, but the complete X-ray data set was not obtained. In attempts to collect a full set, a new complex (**2.10**) was created. The new complex formed under the same reaction conditions previously employed and solved in the monoclinic space group $P2_1/c$. Unlike the previous polymeric structure, **2.10** is a discrete [2+2] macrocycle.

The macrocycle, shown in Figure 2.5, is not completely symmetrical and the asymmetric unit contained a complete macrocycle which consists of two silver atoms, one of which is disordered over two positions, two coordinated counter anions and two molecules of ligand **1.28**.

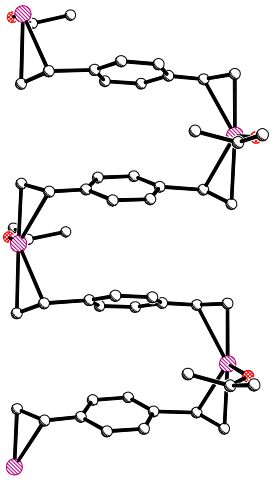


Figure 2.4 *– Previously identified para-divinylbenzene complex with coordinated solvent molecules.*[95] *Hydrogen atoms and counter anions are excluded for clarity.*

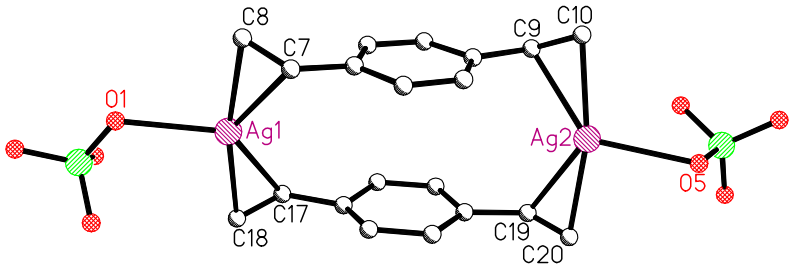
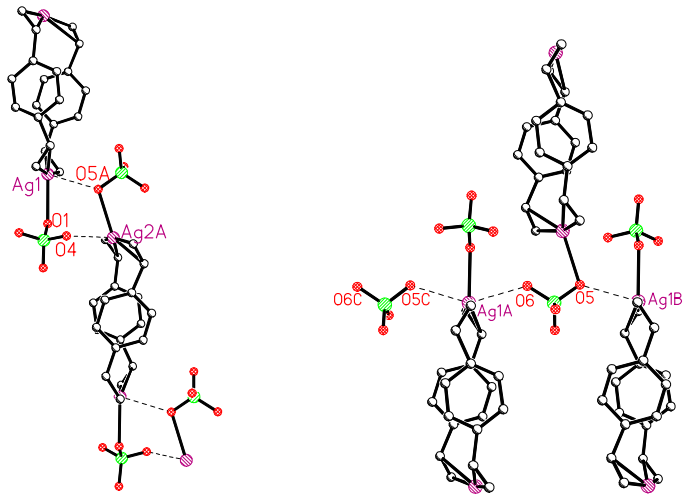


Figure 2.5 *– View of the macrocyclic* ***2.10****. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Ag1-C7 2.474(7), Ag1-C8 2.341(6), Ag1-C7,C8 2.313(7), Ag1-C17 2.45(1), Ag1-C18 2.326(7), Ag1-C17,C18 2.31(1), Ag1-O1 2.488(4), Ag2-C9 2.441(7), Ag2-C10 2.345(8), Ag2-C9,C10 2.300(7), Ag2-C19 2.37(1), Ag2-C20 2.393(9), Ag2-C19,C20 2.33(1), Ag2-O5 2.533(5), C7,C8-Ag1-C17,C18 141.0(4), C7,C8-Ag1-O1 104.9(2), C17,C18-Ag1-O1 104.1(3), C9,C10-Ag2-C19,C20 133.3(4), C9,C10-Ag2-O5 119.8(2), C19,C20-Ag1-O5 101.8(3).*

The silver disorder occurs in Ag2 with a dominant occupancy of 76 %, which is that shown in Figure 2.5. Within the macrocycle the silver atoms are three coordinate with two alkenes and one oxygen atom from the coordinating perchlorate counter anion in the third coordination site. The two silver atoms within the macrocycle are doubly bridged by two molecules of **1.28** and both have a distorted T-shaped geometry with the largest angle occurring between the two alkenes. The Ag···Ag separation across ligand **1.28** is 8.04 Å. The major difference between **2.10** and the previous structure, occurs in the configuration of the two coordinated silver atoms relative to each other. In complex **2.10** they are both on the same side of **1.28** whereas previously they were on opposing sides.



a) ***b)***

Figure 2.6 *– Weak silver(I)-oxygen interactions.* ***a)*** *Pseudo-doubly bridging perchlorate anions, Ag1···O5A 2.70 Å, Ag2A···O4 2.63 Å* ***b)*** *pseudo-singly bridging perchlorate Ag1A···O6 2.74 Å, Ag1B···O5 2.70 Å.*

Weak interactions between silver atoms and the counter anions link the [2+2] macrocycles together into two dimensions. Two perchlorate anions pseudo-doubly bridge the silver atoms, where a perchlorate is bonded to one silver and weakly interacts with the second and vice versa for the second perchlorate, as shown in Figure 2.6(a). Secondly, the macrocycles are also linked together by pseudo-singly bridging perchlorate anions

much in the same manner as just described except through only one bridging perchlorate which is shown in Figure 2.6(b).

2.4 Complexes of 1,4-Diallylbenzene

With silver(I) perchlorate (**2.11**)

Ligand **2.6** gives two different structures when reacted with silver(I) perchlorate and silver(I) trifluoroacetate. However in both complexes, **2.6** acts as a linear bridging unit. Crystals of **2.11** were subjected to X-ray analysis and solved in the orthorhombic space group Pbam. The asymmetric unit of **2.11** contains half a silver atom, half a molecule of **2.6**, an unrefined toluene molecule and half of an unidentified octahedral counter anion, likely resulting from the exchange of perchlorate with the glass vessel.

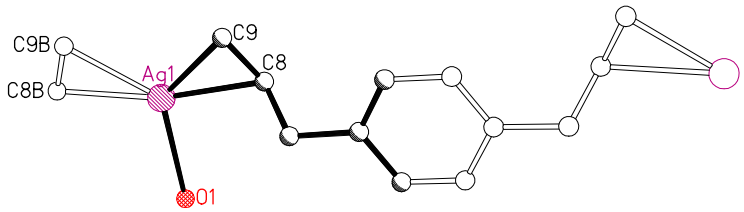
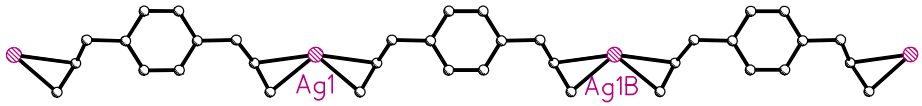


***Figure 2.7** – Core structure of **2.11**. Hydrogen atoms, non-coordinating atoms of the counter anion and the toluene solvate molecule are excluded for clarity. Selected bond lengths (Å) and angles (°): Ag1-C8 2.42(1), Ag1-C9 2.36(2), Ag1-C8,C9 2.28(2), Ag1-O1 2.56(3), O1-Ag1-C8,C9 112.9(5), O1-Ag1-C8B,C9B 112.9(5), C8,C9-Ag1-C8B,C9B 133.6(9).*

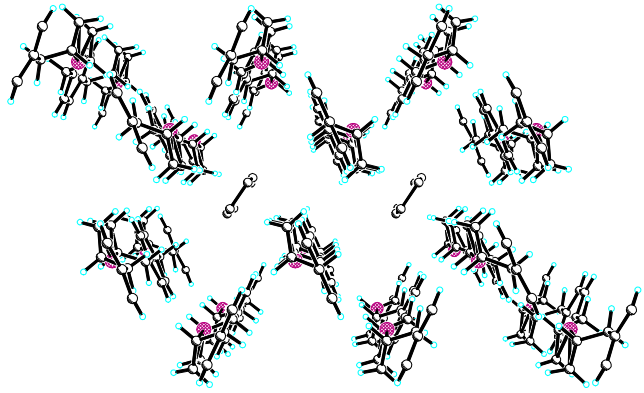
The silver atoms in **2.11** are three coordinate with two olefins and an oxygen atom coordinated and have a distorted trigonal planar geometry. The Ag···Ag separation across ligand **2.6**, with the addition of the carbon atom spacers in both functional arms, is much greater than **1.28** at 11.93 Å.

Similar to **1.28**, ligand **2.6** forms a one-dimensional polymer with silver(I) perchlorate. However with the addition of the single carbon atom spacer in the functional arms ligand

2.6 is now able to bridge silver atoms in a linear manner, see Figure 2.8, unlike **1.28** which forms a zig-zag polymer. The zig-zag shape of the polymer arises from it folding back upon itself to enable off-set π-π stacking interactions between the benzene rings in **1.28**. In **2.11** π-π stacking arises between aromatic rings in different polymer chains reducing the need to fold back upon itself. This is also facilitated by the presence of aromatic toluene in the crystal lattice which contributes to the π-π stacking interactions.



a)



b)

Figure 2.8 *– **a)** View of the linear one-dimensional polymer. Hydrogen atoms and the counter anion have been omitted for clarity. **b)** Edge-to-face π-π stacking between benzene rings in adjacent polymer chains and toluene molecules; only hydrogen atoms on toluene molecules have been excluded.*

With silver(I) trifluoroacetate (**2.12**)

Ligand **2.6** was mixed with silver(I) trifluoroacetate in a 1:1 ratio which gave a crystalline compound (**2.12**) which was suitable for X-ray analysis. The asymmetric unit of this structure, seen in Figure 2.9, is quite complex with four crystallographically independent silver atoms and counter anions as well as two coordinated half molecules of ligand **2.6**.

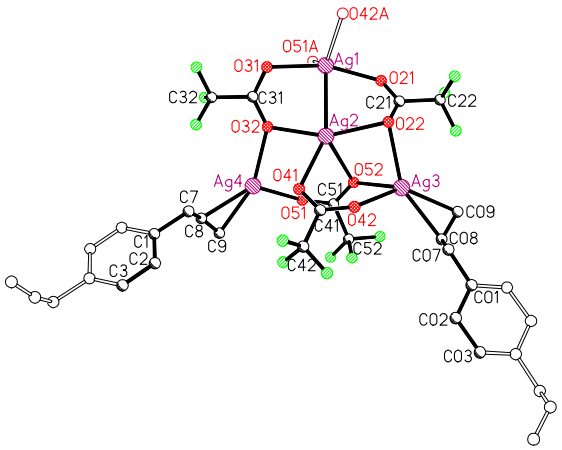
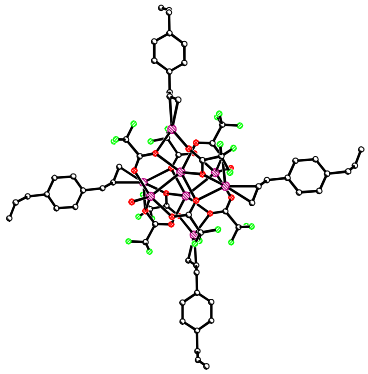


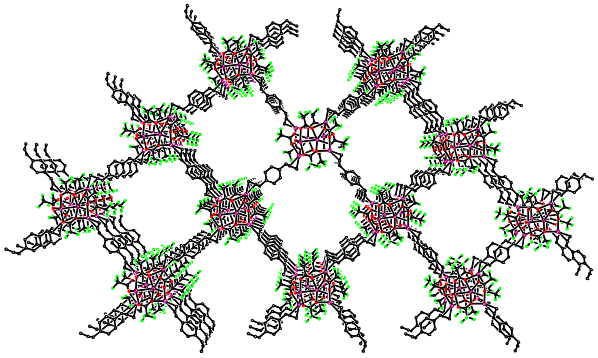
Figure 2.9 *– Asymmetric unit of complex* ***2.12****. Disorder and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O21 2.235(7), Ag1-O31 2.238(7), Ag1-O42A 2.417(7), Ag1-O51A 2.376(7), Ag1-Ag2 2.823(1), Ag2-O22 2.365(6), Ag2-O32 2.326(7), Ag2-O41 2.408(7), Ag2-O52 2.452(7), Ag3-C08 2.40(1), Ag3-C09 2.29(3), Ag3-C08,C09 2.26(3), Ag3-O22 2.476(6), Ag3-O42 2.409(7), Ag3-O52 2.401(7), Ag4-C8 2.33(1), Ag4-C9 2.22(2), Ag4-C8,C9 2.21(2), Ag4-O32 2.303(7), Ag4-O51 2.315(7), O21-Ag1-O31 163.4(3), O21-Ag1-O51A 91.4(2), O21-Ag1-O42A 94.5(3), O21-Ag1-Ag2 80.4(2), O31-Ag1-O42A 99.0(2), O31-Ag1-O51A 88.9(2), O31-Ag1-Ag2 84.6(2), O42A-Ag1-O51 124.2(3), O42A-Ag1-Ag2 119.2(2), O51A-Ag1-Ag2 116.5(2), O22-Ag2-O32 154.5(2), O22-Ag2-O41 122.9(2), O22-Ag2-O52 76.6(2), O22-Ag2-Ag1 79.4(2), O32-Ag2-O41 82.6(2), O32-Ag2-O52 110.7(3), O32-Ag2-Ag1 75.9(2), O41-Ag2-O52 81.0(2), O41-Ag2-Ag1 154.2(2), O52-Ag2-Ag1 119.8(2), O22-Ag3-O42 99.3(2), O22-Ag3-O52 75.5(2), O22-Ag3-C08,C09 139.2(5), O42-Ag3-O52 85.6(2), O42-Ag3-C08,C09 115.1(4), O52-Ag3-C08,C09 126.2(5), O32-Ag4-O51 95.1(3), O32-Ag4-C8,C9 145.6(8), O51-Ag4-C8,C9 117.7(6).*

All of the silver atoms and counter anions are found in a central cluster. Two silver atoms, Ag1 and Ag2, are five coordinate with a short Ag-Ag bond length of 2.82 Å as

well as four additional oxygen atoms from the counter anions coordinated. The geometry about the two silver atoms is similar with both being distorted trigonal bipyramidal. The two other silver atoms, Ag3 and Ag4, both have one alkene from ligand **2.6** coordinated. Ag3 is four coordinate with one alkene and three oxygen atoms from counter anions coordinated and has a calculated τ_4 of 0.67 indicating a see-saw geometry. Ag4 is three coordinate with one alkene and two oxygen atoms coordinated. However there is a longer ranged interaction between Ag4 and O41 (Ag4···O41 261 Å) but this is, by definition, not a silver-oxygen bond. The geometry about Ag4 is distorted trigonal planar. The fluorine atoms on C22 and C32 are disordered over two positions.



a)



b)

Figure 2.10 – a) *Four coordinated molecules of ligand* ***2.6*** *at 90 ° angles to one another* ***b)*** *view of the three-dimensional* ***2.12*** *showing the one-dimensional pores.*

The resulting three-dimensional grid has one-dimensional pores running through with an approximate diameter of 18.8 Å × 18.8 Å, measured from the centres of the silver(I) cluster. Filling this void space is a second interpenetrated three-dimensional grid. The one-dimensional silver(I)-trifluoroacetate polymers of the second grid sit in the pores of the first, as seen in Figure 2.11(a), and the bridging ligand **2.6** alternates between grids with π-π stacking between the benzene cores as seen in Figure 2.11(b).

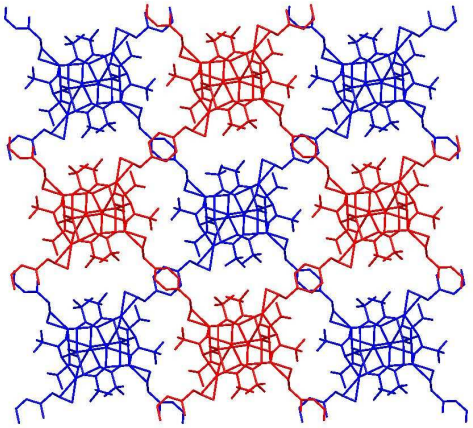
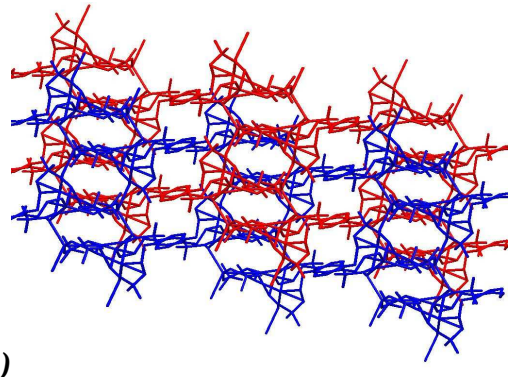
a)   ***b)***

Figure 2.11 *– View of the two interpenetrated three-dimensional grids. Hydrogen atoms have been omitted for clarity.* ***a)*** *The silver-trifluoroacetate polymer of the second grid filling the pore space of the first* ***b)*** *view of interpenetration.*

2.5 Complexes of 1,4-Di(allyloxy)benzene

With silver(I) perchlorate (**2.13**)

Two successful reactions of **2.9** with silver(I) occurred with the perchlorate (**2.13**) and tetrafluoroborate (**2.14**) salts. The influence of the counter anion on the resulting architecture is evident when comparing **2.13** to **2.14**. Complex **2.13** was formed in a chloroform/acetone solvent solution and X-ray analysis revealed the incorporation of acetone into the structure. The asymmetric unit contains one silver atom, a non-coordinated perchlorate counter anion, two symmetrically independent half molecules of **2.9** and a coordinated acetone molecule as seen in Figure 2.12.

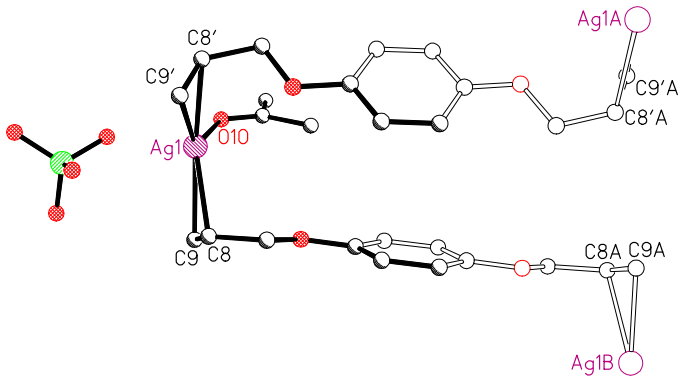


Figure 2.12 *– The asymmetric unit of* ***2.13****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C8 2.474(1), Ag1-C9 2.415(2), Ag1-C8,C9 2.348(2), Ag1-C8' 2.464(2), Ag1-C9' 2.401(2), Ag1-C8',C9' 2.336 (2) Ag1-O10 2.335(1), O10-Ag1-C8,C9 115.27(6), O10-Ag1-C8',C9' 114.72(6), C8,C9-Ag1-C8',C9' 127.09(6).*

Both of the symmetrically independent molecules of **2.9** lie on centres of inversion and bridge two silver atoms through the coordination of the terminal alkenes. Each silver atom has a slightly distorted trigonal planar geometry with two alkenes and one carbonyl oxygen coordinated. The largest angle around the silver atom is between the two alkenes and the slight distortion from trigonal planar geometry likely occurs because of steric repulsion. The perchlorate counter anion has a weak association between one of its oxygen atoms and the silver (2.61 Å). The Ag···Ag separation across the ligand is 11.35 Å which is the longest separation achieved out of the three di(allyloxy)benzene isomers. However it is half an angstrom shorter than the separation seen in complex **2.12** with ligand **2.6**, even though it has an additional atom spacer in each arm. The conformation in which the silver atoms coordinate, can account for the discrepancies between the expected and actual distances. In **2.13**, ligand **2.9** essentially lies on a plane and the silver atoms lie above and below this plane. In **2.11** and **2.12** the silver atoms lie in the same side of the plane, as opposed to opposite sides, giving a longer separation. The two different binding modes are schematically represented in Figure 2.13.

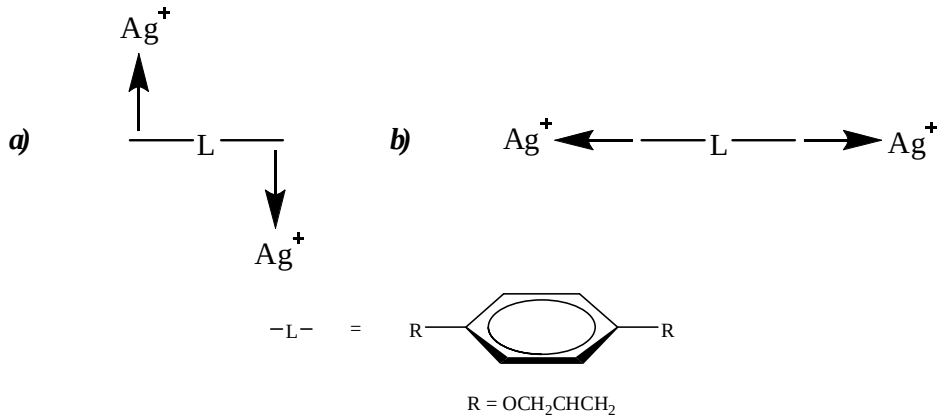
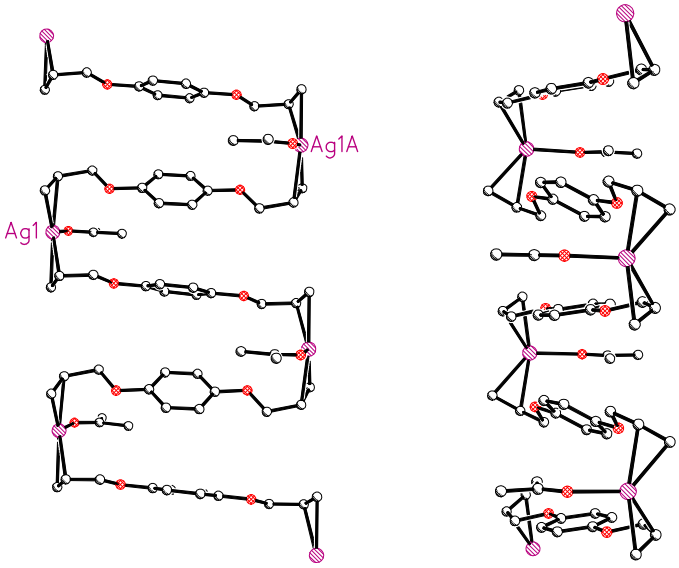


***Figure 2.13** – Schematic representation of different binding modes of silver(I). **a)** Binding mode of ligand **2.9 b)** binding mode of ligand **2.6**.*

The overall structure is a one-dimensional metallopolymer which continuously folds back upon itself as seen in Figure 2.14(a). This is the same motif seen in the reaction of the related ligand **1.28** with silver(I) perchlorate, but now with larger Ag···Ag separations. The benzene rings in ligand **2.9** do not lie flat with respect to one another as steric repulsion from the coordinated acetone causes them to twist, as shown in Figure 2.14(b).



a) ***b)***

***Figure 2.14** – **a)** Folding of the one-dimensional polymer **2.13 b)** view of benzene rings twisting with respect to each other to accommodate coordinated acetone molecules.*

The perchlorate anions give the structure stability by providing a network of weak hydrogen bonding between their oxygen atoms and hydrogen atoms from ligand **2.9** and coordinated acetone molecules (2.52 Å – 2.68 Å). There is additional weak hydrogen bonding between the carbonyl oxygen in the acetone and an olefinic hydrogen on **2.9** (2.54 Å).

With silver(I) tetrafluoroborate (**2.14**)

The second complex of **2.9** was with silver(I) tetrafluoroborate, **2.14**. Single crystal X-ray analysis revealed that in the absence of solvent acetone, a water molecule has coordinated to silver instead. However, while still maintaining a 1:1 ratio of silver to ligand **2.9**, the asymmetric unit, seen in Figure 2.15, now contains two full molecules of **2.9**, two atoms of silver, two non-coordinated tetrafluoroborate anions and one coordinated water molecule. Unlike in **2.13**, water was not in excess and to fill the third coordination site the second silver atom has an η^2 interaction to the benzene ring in the second molecule of **2.9**.

There are two symmetrically independent silver atoms which both have slightly distorted trigonal planar geometry. Ag2 has two alkenes and an oxygen atom from a water molecule and, as in **2.13**, the largest angle is between the two coordinated alkenes. Ag1 has a less distorted trigonal planar geometry and is coordinated to two alkenes and one benzene ring, via an η^2 interaction. The silver to C5',C6' centroid distance is longer than the silver to olefin centroid distance which is consistent with literature reports.[32] The silver to olefin centroid distance in Ag2 is marginally longer than in Ag1, presumably because of the presence of three bulky donors.

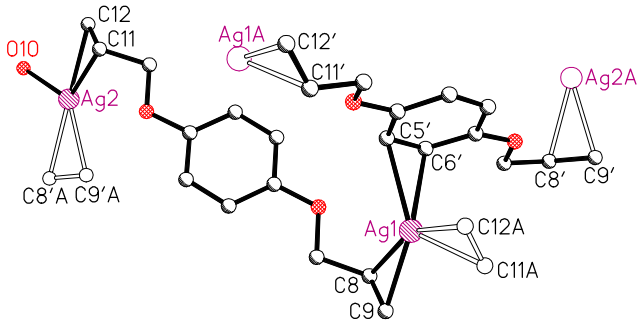


Figure 2.15 *– Asymmetric unit of* ***2.14****. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): Ag1-C5' 2.537(4), Ag1-C6' 2.614(3), Ag1-C5',C6' 2.480(4), Ag1-C8 2.429(4), Ag1-C9 2.390(4), Ag1-C8,C9 2.315(4), Ag1-C11' 2.429(4), Ag1-C12' 2.465(4), Ag1-C11',C12' 2.356(4), Ag2-C8' 2.413(4), Ag2-C9' 2.354(4), Ag2-C8',C9' 2.287 (4), Ag2-C11 2.492(4), Ag2-C12 2.370(4), Ag2-C11,C12 2.339(4), Ag2-O10 2.288(3), C5',C6'-Ag1-C8,C9 116.1(1), C5',C6'-Ag1-C11A,C12A 116.4(1), C8,C9-Ag2-C11A,C12A 124.4(1), O10-Ag2-C8'A,C9'A 118.0(1), O10-Ag2-C11,C12 105.3(1), C8'A,C9'A-Ag2-C11,C12 134.9(1).*

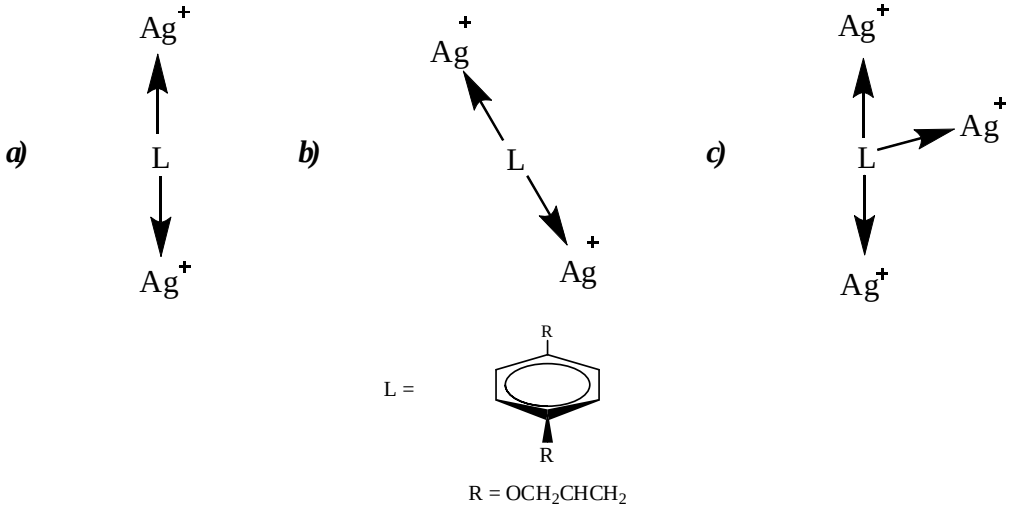


Figure 2.16 *– Schematic representation of different binding modes of silver(I) to the alkenes in ligand* ***2.9****.* ***a)*** *Binding mode of ligand* ***2.9*** *in* ***2.13*** ***b)*** *binding mode of bidentate ligand* ***2.9*** *in* ***2.14*** ***c)*** *binding mode of tridentate ligand* ***2.9*** *in* ***2.14****.*

With the addition of an η^2 interaction in **2.14** a completely different architecture results compared to **2.13**. Ligand **2.9** now has a bidentate and tridentate coordination mode. The bidentate **2.9** bridges two silver atoms through the coordination of both alkenes as in **2.13**. In the tridentate mode, **2.9** bridges two silver atoms as in the bidentate ligand and the third silver is coordinated by an η^2 interaction with the benzene ring. The Ag···Ag separation across the bidentate ligand is 11.83 Å, Ag1···Ag2 in Figure 2.17(a), and is about half an angstrom longer than in **2.13**. The tridentate ligand has a shorter Ag···Ag separation across the two silver atoms coordinated to the alkenes, Ag1A and Ag2A (Figure 2.17(b)), with a distance of 10.62 Å, The variations in the Ag···Ag separations demonstrate the flexible nature of the allyl ether arms and the different conformations of silver coordination are shown in Figure 2.16. The asymmetrical conformation of the allyl ether arms in the tridentate **2.9** is reflected in the two different distances of 6.43 Å and 7.22 Å between Ag1···Ag1A and Ag1···Ag2A in Figure 2.17(b), respectively.

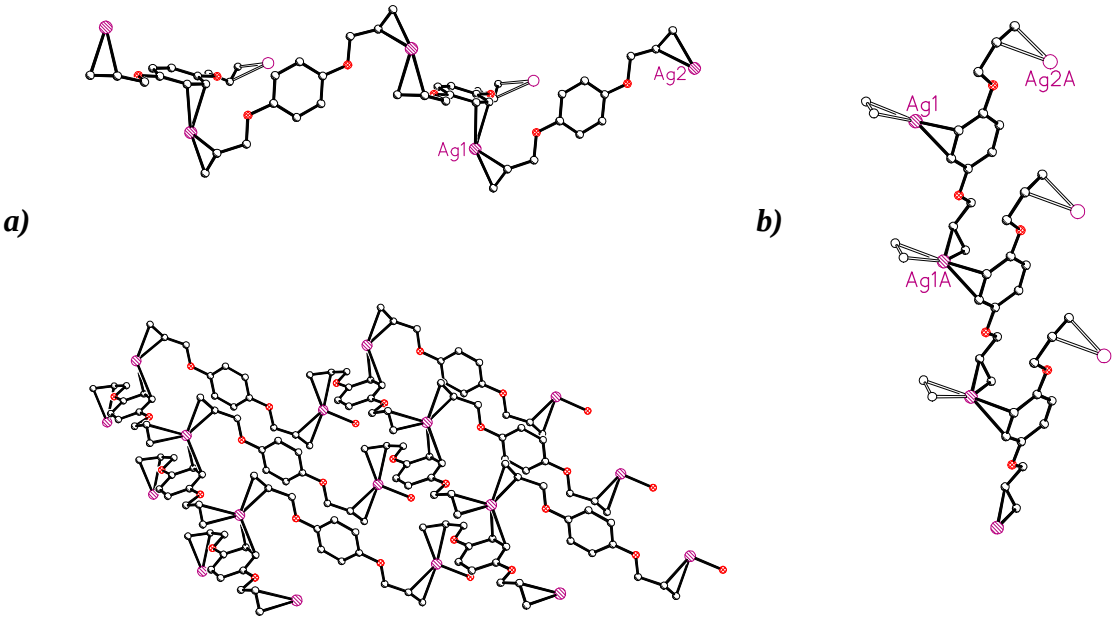


Figure 2.17 *– **a)** One direction of polymer propagation **b)** second direction of polymer propagation **c)** view of a section of the two-dimensional metallopolymer.*

Complex **2.14** is a two-dimensional metallopolymer. Figure 2.17(a) shows the metallopolymer propagating in one direction through the bridging of silver by **2.9** alternating between bridging though both terminal alkenes and then through the alkene and the η^2 interaction on the benzene ring of a second ligand of **2.9**. The other direction of propagation, seen in Figure 2.17(b), is through the repeated bridging of silver by one terminal alkene and then through to the η^2 interaction on the same ligand. Figure 2.17(c) shows the overall two-dimensional metallopolymer.

The two-dimensional sheets stack in a ABAB manner with weak hydrogen bonding between the fluorine atoms on both crystallographic tetrafluoroborate counter anions and hydrogen atoms on both bidentate and tridentate **2.9** (2.37 – 2.59 Å).

2.6 Complexes of 1,3-Diallylbenzene

Complexes with silver(I) and ligand **2.5** were not formed. This was hampered by the small quantities of **2.5** produced and further work may still yield results.

2.7 Complexes of 1,3-Di(allyloxy)benzene

With silver(I) hexafluorosilicate (**2.15**)

The formation of complex **2.15** was somewhat serendipitous as the original solution contained ligand **2.8** and silver(I) hexafluorophosphate. The hexafluorophosphate decomposed resulting in HF which attacked the glass vial giving the slow release of hexafluorosilicate. This enabled the slow formation of a small quantity of crystalline **2.15**. An independent experiment with equal measures of **2.8** and silver(I) perchlorate with excess ammonium hexafluorosilicate did not yield any product as the ammonium hexafluorosilicate was too insoluble. Single crystal X-ray diffraction was performed and the structure solved in the triclinic space group P-1. The asymmetric unit which is shown in Figure 2.18, contains one full molecule of **2.8**, two crystallographically independent silver atoms, three coordinated water molecules and one hexafluorosilicate counter anion.

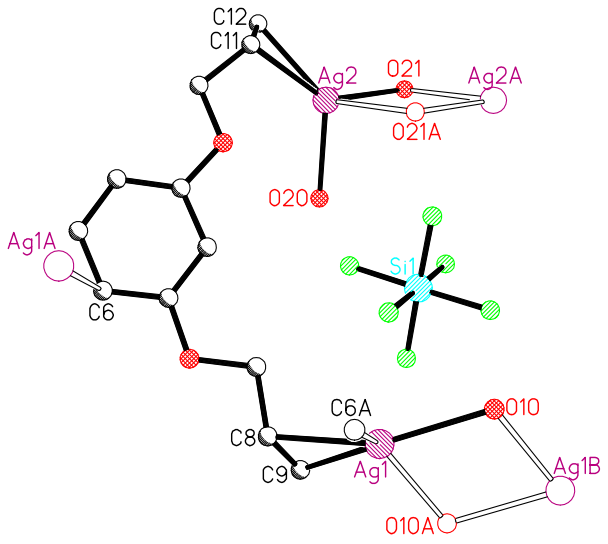


Figure 2.18 *- The asymmetric unit of* ***2.15****. Hydrogen atoms have been excluded for clarity. Selected bond lengths (Å) and angles (°): Ag1-C6A 2.593(3), Ag1-C8 2.468(3), Ag1-C9 2.429(3), Ag1-C8,C9 2.356(3), Ag1-O10 2.490(2), Ag1-O10A 2.408(2), Ag2-C11 2.368(3), Ag2-C12 2.331(3), Ag2-C11,C12 2.252(3), Ag2-O20 2.306(2), Ag2-O21 2.394(2), Ag2-O21A 2.468(2), O10-Ag1-O10A 74.51(8), O10-Ag1-C6A 86.43(7), O10-Ag1-C8,C9 159.44(9), O10A-Ag1-C6A 126.49(8), O10-Ag1-C8,C9 103.80(9), C6A-Ag1-C8,C9 109.66(1), O20-Ag2-O21 92.61(8), O20-Ag2-O21A 93.33(8), O21-Ag2-O21A 76.38(8), O21-Ag2-C11,C12 129.19(9), O21A-Ag2-C11,C12 119.83(9), O20-Ag2-C11,C12 129.7(1).*

Both of the two crystallographically independent silver atoms are four coordinate. Ag1 has two water molecules, one alkene and an η^1 benzene coordinated and Ag2 has three water molecules and one alkene coordinated. The calculated τ_4 for Ag1 is 0.53 and 0.72 for Ag2 implying a see-saw geometry. Both Ag1 and Ag2 are doubly bridged by two water molecules to form $Ag_2(H_2O)_2$ units where both silver atoms within a unit are either of the type Ag1 or Ag2. The C=C centroid to silver distance is much shorter in Ag2 than it is in Ag1 as seen in **2.12** which has silver with only one alkene coordinated. Evidence pointing to the central atom in the counter anion being a silicon is an improved

refinement and the fact that the Si-F bond lengths range between 1.662(2) - 1.689(2) Å which is longer than expected of P-F bond lengths, which are between 1.565(4) - 1.621(1) Å.[†] Additionally there is only one counter anion per two silver(I) atoms which is consistent with a 2^- charge.

Ligand **2.8** is coordinated to three silver atoms, two via the terminal alkenes and the third through an η^1 interaction within the benzene ring. The manner in which **2.8** interacts with silver(I) is more analogous to **1.27**, shown in Figure 2.19, than the corresponding *meta*-divinylbenzene which only acts as a bidentate ligand.

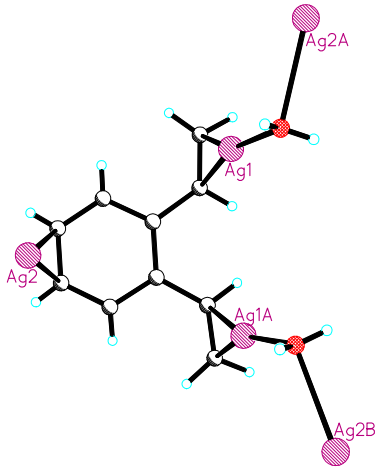
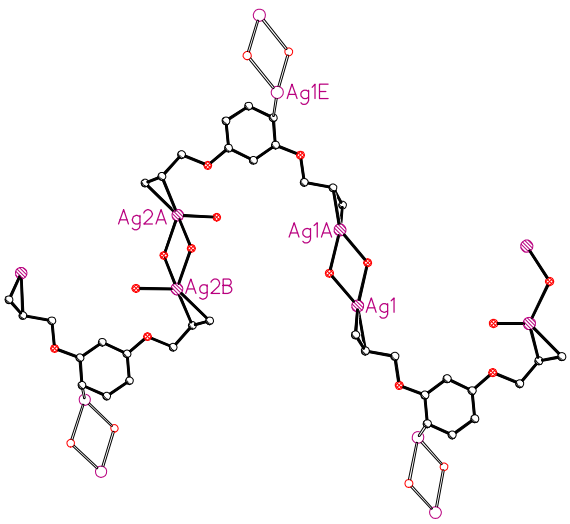


Figure 2.19 *– View of ligand **1.27** interacting with three silver atoms in a silver(I) perchlorate complex. The perchlorate counter anions have been excluded for clarity.*

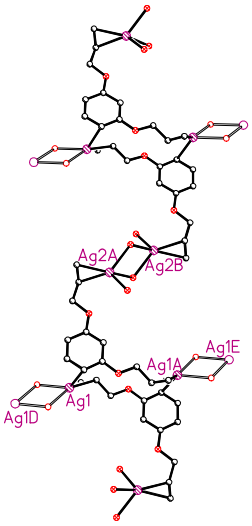
Similar to the silver(I) complex with **1.27**, ligand **2.8** also forms a two-dimensional metallopolymer with silver(I). One direction of polymer propagation is comprised by the bridging of $(Ag1)_2(H_2O)_2$ units to $(Ag2)_2(H_2O)_2$ units by ligand **2.8** through the coordination of both the olefins as seen in Figure 2.20(a). The second direction of propagation is a little more complicated and it occurs by the bridging of $(Ag2)_2(H_2O)_2$ units to Ag1 by ligand **2.8** through an allyl ether arm and the benzene ring. Ag1 is then

[†] P-F bond lengths were taken from a PF_6^- counter anion in complex **2.17**, **4.22** and **5.12**.

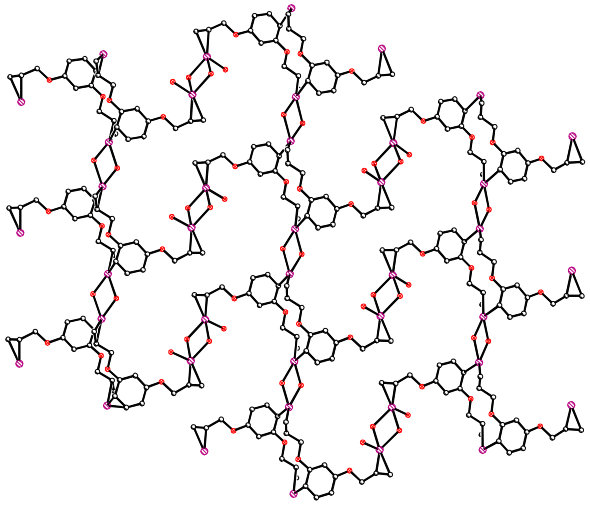
bridged back to the next $(Ag2)_2(H_2O)_2$ by a second molecule of **2.8** as shown in Figure 2.20(b). The Ag···Ag separation across the*meta* allyl ether arms, Ag1A to Ag2A (Figure 2.20(a)), is 8.45 Å and is longer than the Ag···Agseparation seen in the complexes of the *ortho* di(allyloxy)benzene isomer **2.7** and shorter than the *para* isomer **2.9**.



a)



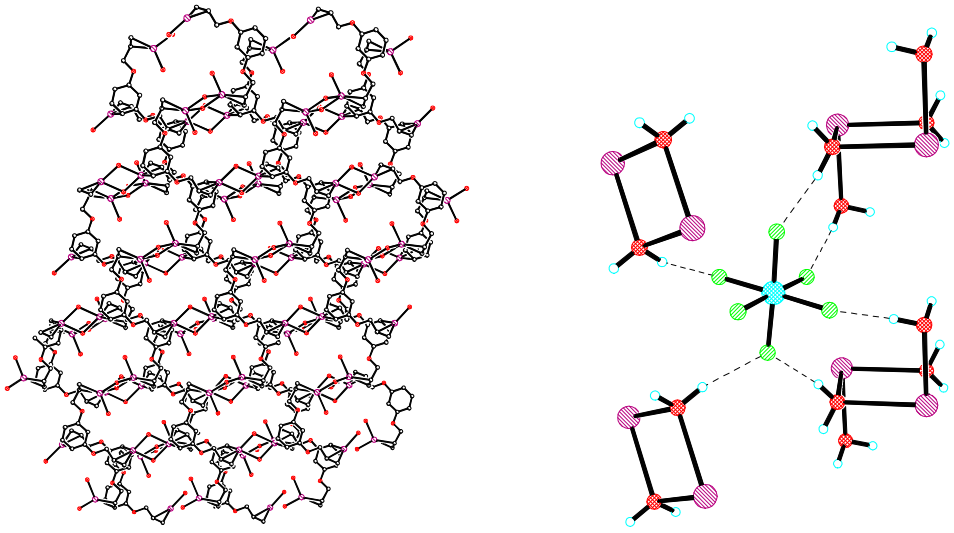
b)



c)

Figure 2.20 – a) *One direction of polymer propagation* ***b)*** *view of the second direction of polymer propagation* ***c)*** *view of the overall two-dimensional network.*

The two-dimensional sheets stack upon each other in an ABAB manner which creates one-dimensional channels as shown in Figure 2.21(a). The channels are hydrophilic, as water molecules line them, and they are filled with the hexafluorosilicate counter anions. The counter anion is held in place with hydrogen bonding, where each hexafluorosilicate anion has six hydrogen bonds which occur from its fluorine atoms to the hydrogen atoms on the coordinated water molecules, as shown in Figure 2.21(b). The O-H···F distances range from 1.82 Å to 1.97 Å. The hydrogen bonds not only hold the anion in place, but also serve to link the two-dimensional sheets together.



a) ***b)***

Figure 2.21 – a) *View of the one-dimensional hydrophilic channels* ***b)*** *view of the six hydrogen bonds tethering the hexafluorosilicate anion in place.*

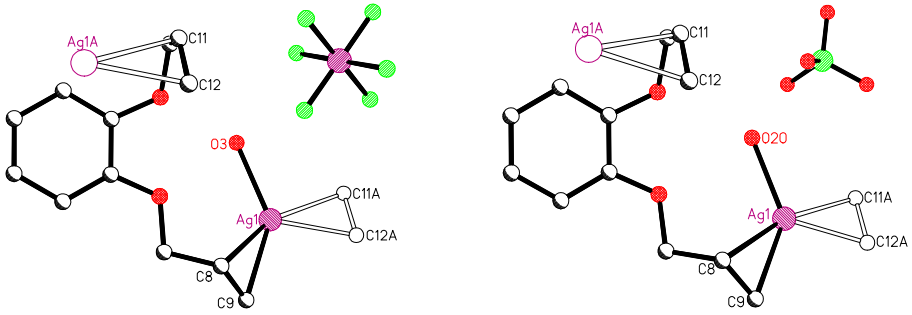
2.8 Complexes of 1,2-Diallylbenzene

Although ligand **2.4** was mixed with a variety of silver(I) salts no complexes were isolated. One possibility is that **1.26** is less rigid and is not constrained to one conformation making it less likely to crystallise. Alternatively, ligand **2.7**, which has more flexibility, consistently forms one-dimensional helical coordination polymers, (*vide infra*) and ligand **2.4** may not be flexible enough to accommodate this favoured motif.

2.9 Complexes of 1,2-Di(allyloxy)benzene

With silver(I) perchlorate (**2.16**), hexafluorophosphate (**2.17**)

Ligand **2.7** was reacted with silver(I) perchlorate (**2.16**), hexafluorophosphate (**2.17**) and triflate (**2.18**). All three reactions carried out at the cooler temperature of 5 °C and yielded crystalline solids suitable for single crystal X-ray analysis. Both **2.16** and **2.17** solved in the triclinic space group P-1 and are isomorphous. As shown in Figure 2.22, the asymmetric units of both complexes are similar with one molecule of **2.7**, one silver atom, a non-coordinated counter anion and a coordinated water molecule.



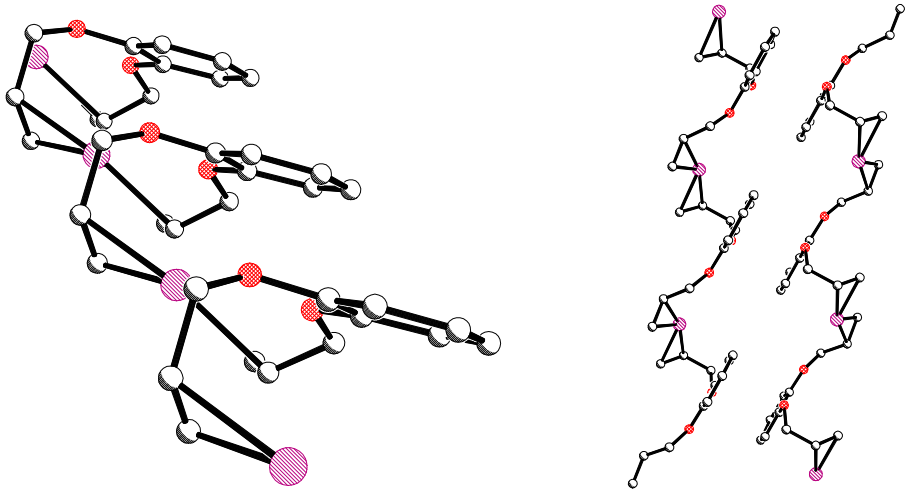
a) ***b)***

Figure 2.22 *– Asymmetric unit of **2.7** with silver(I) hexafluorophosphate and perchlorate. Hydrogen atoms have been excluded for clarity.* ***a)*** *Complex **2.17**, selected bond lengths (Å) and angles (°): Ag1-C8 2.408(2), Ag1-C9 2.368(2), Ag1-C8,C9 2.293(2), Ag1-C11 2.463(2), Ag1-C12 2.426(2), Ag1-C11,C12 2.350(), Ag1-O3 2.282(1), O3-Ag1-C8,C9 121.69(7), O3-Ag1-C11,C12 106.38(6), C8,C9-Ag1-C11,C12 129.45(8)* ***b)*** *Complex **2.16**, selected bond lengths (Å) and angles (°): Ag1-C8 2.405(2), Ag1-C9 2.354(2), Ag1-C8,C9 2.282(2), Ag1-C11 2.465(2), Ag1-C12 2.425(2), Ag1-C11,C12 2.350(2), Ag1-O20 2.260(2), O20-Ag1-C8,C9 118.06(8), O20-Ag1-C11,C12 107.57(8), C8,C9-Ag1-C11,C12 134.08(8).*

The silver atoms in both complexes are three coordinate with two alkenes coordinated and an additional water molecule acting as an auxiliary ligand. The silver has a distorted trigonal planar geometry with a slightly larger angle between the two coordinated alkenes and alternatively a slightly smaller angle between one olefin and the oxygen of the water

molecule (C11,C12-Ag1-O20). Each molecule of **2.7** is coordinated to two different silver atoms through the alkenes and is not chelating as might be expected.

The Ag···Ag separation across the ligand from Ag1··Ag1A is very similar between polymorphs at 7.38 Å and 7.31 Å for **2.16** and **2.17** respectively. This distance is shorter than the separation across both of the other two di(allyloxy)benzene isomers and also the *para*-divinyl and diallylbenzene. It is much longer than the Ag···Ag separation across the vinyl arms in the silver(I) complex of **1.26** as is expected due to the two additional spacer atoms in the functional arms.



a) ***b)***

Figure 2.23 *– View of one-dimensional metallopolymers* ***2.16*** *and* ***2.17****. Hydrogen atoms, counter anions and water molecules have been omitted for clarity.* ***a)*** *Helical nature of the metallopolymer* ***b)*** *π-π stacking between P and M helices.*

Unlike the two-dimensional metallopolymer formed with silver(I) perchlorate and **1.26** both **2.16** and **2.17** are one-dimensional helical coordination polymers with their helical nature shown in Figure 2.23(a). Each crystal is a racemate with both the M and the P forms within a single crystal. M and P forms pair up with π-π stacking (3.28 Å) between them, as seen in Figure 2.23(b). Overall the helical stands pack in the remaining two

dimensions alternating between M and P forms. There is also hydrogen bonding interactions between the water molecule and counter anions with distances of 2.08 Å in **2.16** and 2.29 Å in **2.17**.

With silver(I) triflate (**2.18**)

The complex from the reaction of **2.7** and silver(I) triflate is different in subtle, and not so subtle ways. This structure solved in a higher symmetry space group $P2_1/c$ with one molecule of **2.7** as well as one silver atom and its triflate counter anion in the asymmetric unit, which is shown in Figure 2.24.

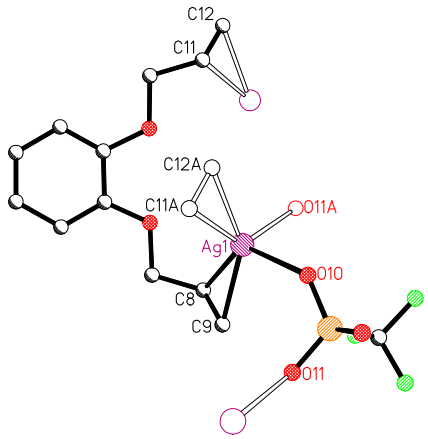


Figure 2.24 *– Asymmetric unit of* ***2.18****. Hydrogen atoms have been excluded for clarity. Selected bond lengths (Å) and angles (°): Ag1-C8 2.469(9), Ag1-C9 2.414(9), Ag1-C8,C9 2.348(9), Ag1-C11 2.444(9), Ag1-C12 2.424(9), Ag1-C11,C12 2.341(9), Ag1-O10 2.388(6), Ag1-O11 2.329(6), O10-Ag1-O11 98.9(2), O10-Ag11-C8,C9 114.2(3), O10-Ag11-C11,C12 92.4(3), O11-Ag11-C8,C9 96.7(3), O11-Ag11-C11,C12 116.9(3), C8,C9-Ag1-C11,C12 133.5(3).*

The coordinated water molecule has been replaced by an oxygen atom from the triflate counter anion and there is also a second additional oxygen coordinated. The silver atoms are now four coordinate with two olefins and two oxygen atoms coordinated. The calculated τ_4 value is 0.77 indicating a geometry between a see-saw and distorted trigonal

pyramidal. The ligand-silver connectivity is very similar in **2.18** to **2.16** and **2.17** with ligand **2.7** bridging silver atoms in a helical manner to form a one-dimensional helical coordination polymer. The major difference between **2.18** and the previous two complexes arises from the exchange of the coordinated water molecule for a coordinated triflate anion. The triflate anion, in addition to ligand **2.7**, bridges silver atoms through two of its oxygen atoms as shown in Figure 2.25. As the allyl ether arms are flexible, they can change their solid state conformation (Figure 2.26(a)) to accommodate the bridging triflate anion. This considerably shortens the Ag···Ag separation from ~7.35 Å in **2.16** and **2.17** to 5.26 Å.

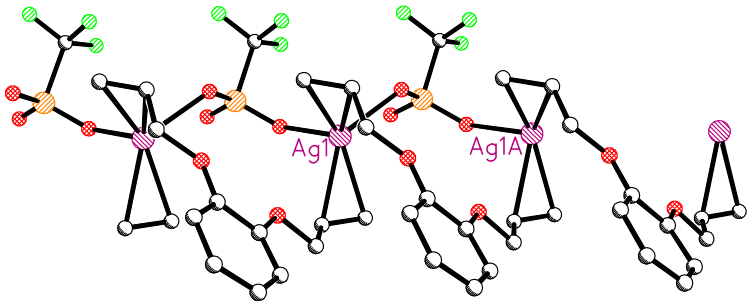
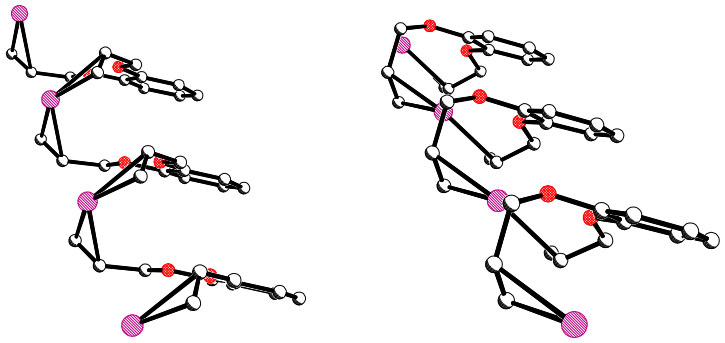
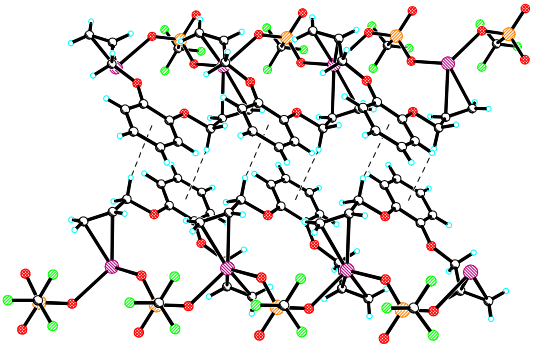


Figure 2.25 *– Section of the one-dimensional polymer* ***2.18****.*

As in **2.16** and **2.17**, there are both P and M helices within the same crystal of **2.18** and they also pair together as in **2.16** and **2.17**. However they interact with each other through CH/π interactions (Figure 2.26(b)) as opposed to offset π-π stacking. With no water molecules present there is no strong hydrogen bonding but there are weak CH···F, 2.50 Å, and CH···O, 2.68 Å, bonds between the fluorine and oxygen atoms in the triflate anion and hydrogen atoms in **2.7** in adjacent polymer chains.



a)



b)

Figure 2.26 – a) *Comparison of ligand conformations in* ***2.18*** *(left) and* ***2.16*** *and* ***2.17*** *(right)* ***b)*** *CH/π interactions between P and M pairs.*

2.10 Nuclear Magnetic Resonance Titrations

Ligand **2.7** was chosen as the solid state structures of its complexes with $AgClO_4$ (**2.16**), $AgPF_6$ (**2.17**) and $AgCF_3SO_3$ (**2.18**) are known and are similar in structure. Additionally all three complexes have suitable solubility in deuterated acetone. Deuterated acetone was selected as significant shifts in the olefinic proton signals were seen and there is no solvent competition as would occur in solvent systems such as deuterated acetonitrile. A ^{1}H NMR spectrum of 1mmol of the free ligand in deuterated acetone was taken at the start of each experiment and acts as the zero. Half mole equivalents of the silver(I) salt was added and allowed five minutes to equilibrate before the next spectrum was taken. This process was repeated until six mole equivalents of the silver(I) salt had been added. The volume of solvent was kept consistent throughout, as the magnitude of the shifts is

dependent on concentration as shown in Figure 2.27(b). The three olefinic protons signals are monitored and are labelled Ha, Ha' and Hb as in Figure 2.27(a).

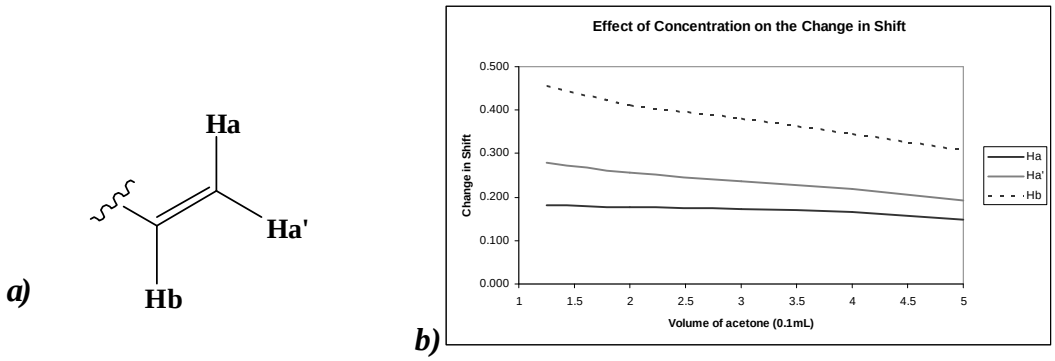


***Figure 2.27** – **a)** Labelling of the olefinic hydrogen atoms **b)** dependence of the chemical shift on the concentration.*

The results for ligand **2.7** with increasing ratios of silver(I) perchlorate is shown in Figure 2.28. There are significant downfield changes in the chemical shift, with the greatest seen in the Hb proton and the least in the Ha proton. This confirms the presence of Ag^{+}.**2.7** species in solution, although the nature of these species cannot be determined. The slope of the graph is curved for all three protons and starts to level off at four equivalents of $AgClO_4$ representing an equilibrium between free and coordinated **2.7**. A 1 mmol sample of the solid complex **2.16** was dissolved in the same volume of dueterated acetone and the change in chemical shift corresponded to a 1:1 silver(I) to ligand ratio on the graph in Figure 2.28. This is also in agreement with the X-ray crystal structure of **2.16** which has a 1:1 ratio.

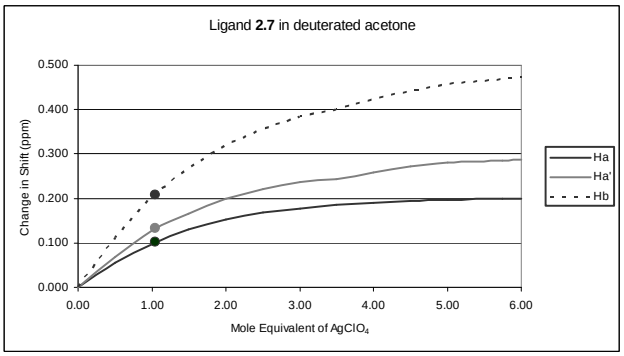


***Figure 2.28** – The change in chemical shifts of the olefinic protons in **2.7** with increasing concentrations of $AgClO_4$.*

The changes in chemical shift in each individual olefinic proton from **2.7** with $AgPF_6$ and $AgCF_3SO_3$ and are plotted alongside $AgClO_4$ in Figure 2.29. $AgClO_4$ and $AgCF_3SO_3$ give very similar results and $AgPF_6$ gives a much gentler slope and does not have as great a change in chemical shift. A possible explanation for this is that the triflate and perchlorate counter anions are coordinating while hexafluorophosphate is not, and although the perchlorate counter anion is non-coordinating in the solid state it probably plays a more significant role in solution.

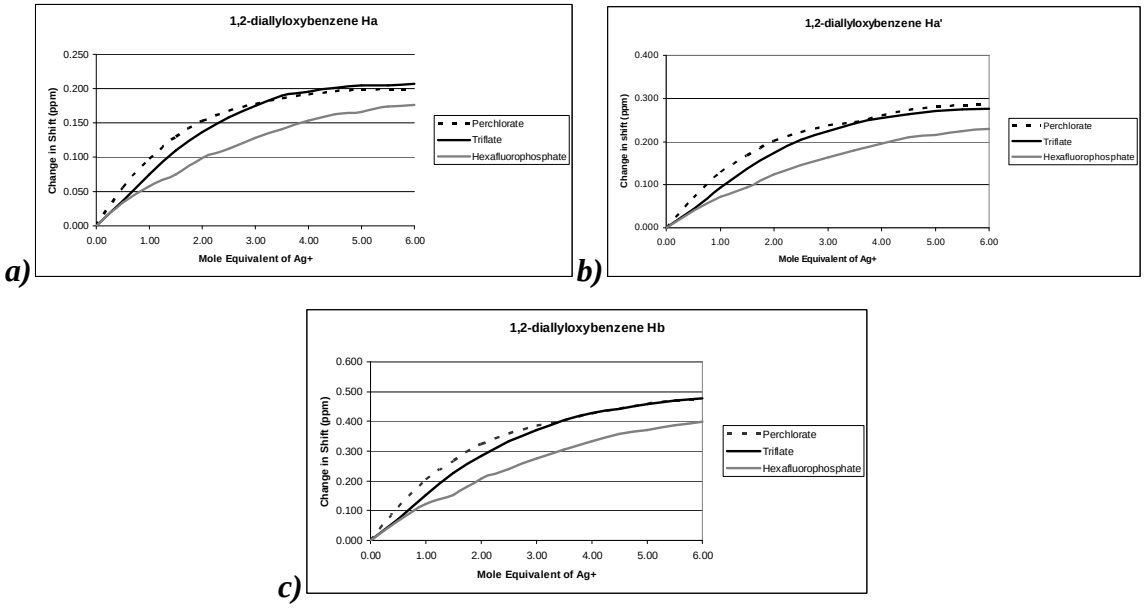


***Figure 2.29** – Comparison of the change in chemical shifts of olefinic protons in **2.6** with $AgPF_6$, $AgCF_3SO_3$ and $AgClO_4$. **a)** Proton Ha **b)** proton Ha' **c)** proton Hb.*

The change in shift starts to level off at four equivalents for all three silver(I) salts. This is in contrast to their solid state ratios of 1:1 indicating that the complexes are in equilibrium with the free ligand.

2.11 Summary

This chapter covers the coordination chemistry of seven disubstituted benzene ligands with various silver(I) salts. Ligand **1.28** was synthesised from a Wittig reaction with

terephathalic aldehyde. Ligands **2.4 – 2.6** were created through simple Stille coupling reactions and ligands **2.7 – 2.9** were prepared from the allylation of dihydroxybenzenes. Only ligand **2.5** was a previously unreported compound.

Ligands **1.28**, **2.6** and **2.9** gave one-dimensional polymers with $AgClO_4$. Both **1.28** and **2.9** gave very similar one-dimensional polymers that continuously folds back upon themselves to enable π-π stacking interactions between the aromatic ligand cores. Alternatively, ligand **2.6** gave a linear one-dimensional polymer which was enabled, in part, by the increase of flexibility of the functional arm. The other factor influencing the formation of the linear polymer is the solvent toluene molecules in the crystal lattice which reduces the need for the polymer to fold as it provides additional π-π stacking interactions. With a change in counter anion from perchlorate to tetrafluoroborate, ligand **2.9** gave a two-dimensional polymer, with **2.9** acting in a bi- and tri-dentate manner. Similarly on changing from a perchlorate to trifluoroacetate counter anion, ligand **2.6** gave a three-dimensional interpenetrated network. Ligand **1.28** gives a second polymorph with $AgClO_4$ and not only forms a one-dimensional polymer, but also a [2+2] macrocycle.

Ligand **2.8** interacts in a tridentate manner with silver(I) which is more analogous to *ortho*-divinylbenzene as opposed to the corresponding *meta*-divinylbenzene. Similar to *ortho*-divinylbenzene, **2.8** forms a two-dimensional metallopolymer. The two-dimensional sheets stack in a way which creates one-dimensional hydrophilic pores which are filled with hexafluorosilicate counter anions.

Ligand **2.7**, as a result of the additional flexibility in the functional arms, gives rise to helical one-dimensional polymers as opposed to the more rigid **1.26**, which gives a two-dimensional network. Remarkably ligand **2.7** has the same solid state conformation with both $AgClO_4$ and $AgPF_6$ and, although in a different conformation, gives a related one-dimensional helical polymer with $AgCF_3SO_3$.

Silver(I)-olefin species are detectable in solution and the silver(I) to ligand ratio of the solid complex is determinable. The exact nature of the species present in solution is unknown, however, it is clear there is an equilibrium between the coordinated and free ligand. The nature of the equilibrium has shown a dependency on the counter anion present.

Chapter Three

Two Armed Ligands with Naphthalene Cores

CHAPTER 3

Two Armed Ligands with Naphthalene Cores

3.1 Introduction

An advantageous feature of metallosupramolecular chemistry is the ability to control the dimensions and geometry of the basic components to give the desired product. The previous chapter explored the effects of using small spacer groups and substitution patterns around a benzene core. Another way to affect the separation of functional groups is to change the core itself. There are many different potential ligand cores from single atoms such as carbon, nitrogen or oxygen to large extended aromatic systems.[109-111] Naphthalene is an effective core as it offers ten possible disubstituted isomers compared to the three (*ortho*, *meta*, *para)* isomers of disubstituted benzene.

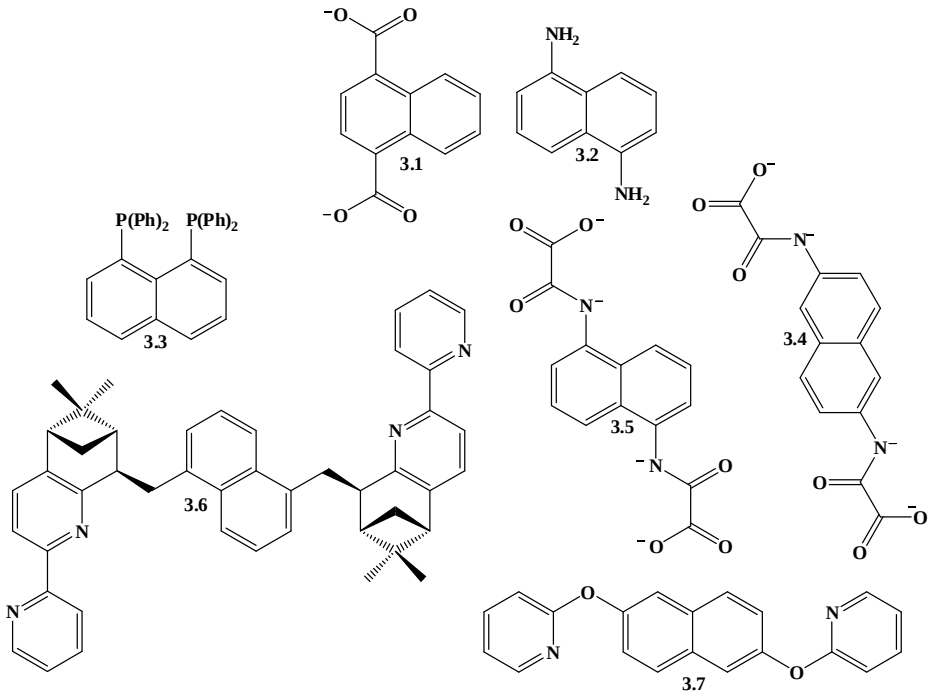


Figure 3.1 *– A selection of ligands with a variety of functional groups and spacers based on a naphthalene core.*

Naphthalene has been successfully used as a core in bisubstituted ligands with a variety of functional groups. Shown in Figure 3.1 are some such examples.[112-117] Ligand **3.1** is used as a simple bridging co-ligand with 2,2'-dipyridylamine to form a dimeric copper complex where the dimers are linked together into a two-dimensional network via hydrogen bonding.[112] It was again used as a bridging co-ligand in a different study, this time with 4,4'-bipyridine, which resulted in a two-dimensional square grid when reacted with Ni(II) or Co(II).[118] Molecule **3.2** has been used as a bridging ligand to bridge two Cu(I)(trifac)$_2$ (trifac = 1,1,1-trifluoropentane-2,4-dionato) units[113] and ligand **3.3** can chelate to Au(II) to form dinuclear gold complexes.[114,115]

Ligand **3.5** has been used, in combination with copper, to form a tetraanionic dinuclear Cu(II) metallacyclophane complex.[117] The intermetallic distance in the complex was calculated to be 8.3 Å. Further calculations showed that the estimated intermetallic distance in an analogous complex using ligand **3.4** would be 10.09 Å. This is representative of the ability to control metal-metal separation through ligand substitution patterns around a naphthalene ring.

Ligand **3.6** is chiral and has been used by Bernardinelli et al. to form chirally predetermined helicates. It was combined with Ag(I) to give two intertwined single-stranded helicates that form an infinite, highly symmetric double helix.[119]

Ligand **3.7** is of particular note as it is one of a series of disubstituted isomers based around a naphthalene core. It has the same 180 ° geometry as an analogous 1,4 disubstituted benzene and both result in a dimetallocyclophane when combined with silver(I) nitrate.[116,120] The metal-metal separation is extended from 10.38 Å in the benzene derived dimetallocyclophane to 12.58 Å by the incorporation of a naphthalene core into the ligand.

Also of interest is that the solid state structure of species produced from this ligand series showed a remarkable dependence on the specific substitution patterns in the naphthalene core. As previously mentioned **3.7**, when combined with silver(I) nitrate, gives a M_2L_2

dimetallocycle and the 1,3-isomer will also give rise to a M_2L_2 dimetallocycle. However using the same silver salt the, 1,5- and 1,6-isomer give one-dimensional zig-zag metallopolymers of a similar nature, and the 1,7-isomer yielded a one-dimensional single-stranded helicate.[116]

With naphthalene's larger aromatic system, there is greater potential for η^2 arene-silver(I) coordination to occur as any electron cloud perturbation introduced by the coordination of silver(I) can effectively be spread more over a two ring system than a one ring system.[121] This offers the opportunity to evaluate the comparative favourability of forming a silver(I)-alkene, silver(I)-arene or a silver(I)-ether oxygen interaction.

Unlike benzene, naphthalene does not have uniform carbon-carbon bond lengths. Naphthalene has three resonance contributors, as shown in Figure 3.2. Two of the resonance contributors have double bonds localised between C1-C2, C3-C4, C5-C6 and C7-C8 with only one resonance contributor where the double bonds are localised between C1-C8a, C2-C3, C4-C4a, C4a-C5, C6-C7 and C8-C8a. This results in the bonds between carbons with the double bond localised in two contributors having shorter lengths compared to carbons with double bonds localised in only one contributor. The shorter bond lengths are generally 1.37 Å and the longer lengths 1.42 Å.

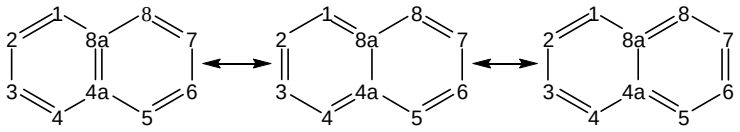
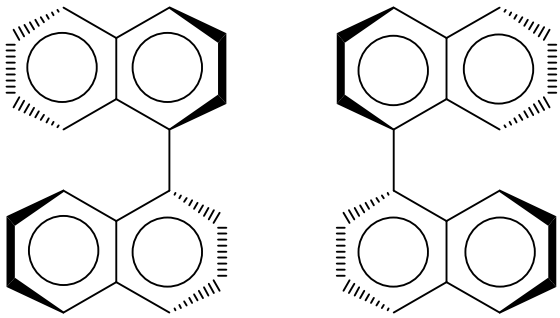


Figure 3.2 *– Three resonance contributors of naphthalene.*

Theoretical calculations based on delocalization energies done in the early 1960's by Fukui et al. predict silver will preferentially coordinate to naphthalene at the C1-C2, C3-C4, C5-C6 and C7-C8 positions.[122] The first crystal structure of a naphthalene silver(I) complex was published in 1969 revealing naphthalene bridging four silver atoms via η^2 coordination at all four of the predicted positions.[121,123] A search of the CCD yielded two silver(I) complexes of disubstituted naphthalenes with η^2 silver coordinated at the

predicted positions[124] and one monosubstituted naphthalene with η^2 coordination at the unexpected position of the C2-C3 bond.[125]

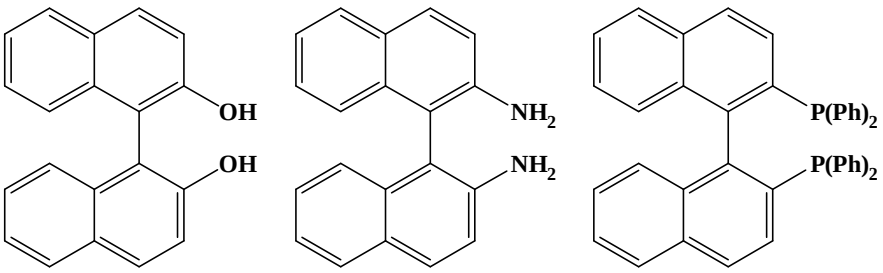
The ability to incorporate chirality into assemblies is an important aspect of metallosupramolecular chemistry. Chirality can be achieved with either the ligand or metal component or a combination of both. Most commonly it is incorporated through the use of chiral ligands. Chiral ligands can arise from either modified natural products like **3.6** or the resolution of synthetic compounds like 1,1'-binaphthalene.



(R)-(+)- (S)-(-)-

Figure 3.3 *– Enantiomers of 1,1'-Binaphthalene.*

1,1'-Binaphthalene has axial chirality as a result of restricted rotation around the transannular bond. This unit is used as a ligand core with substitution at the 2,2'-position. Substitution at this position with oxygen gives 1,1'-binaphthyl-2,2'-diol (BINOL), nitrogen gives 2,2'-diamino-1,1'-binaphthyl- (BINAM) and diphenylphosphine gives 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP).



BINOL BINAM BINAP

These compounds and in particular BINOL and BINAP are among the most widely used ligands for both stoichiometric and catalytic asymmetric reactions in recent times.[126,127] BINOL and BINAM are used routinely in metallosupramolecular chemistry.[128]

BINOL is widely used in metallosupramolecular chemistry as it can be functionalized on the naphthalene ring, the hydroxyl groups or both.[128] Some examples of assemblies arising from ligands with a BINOL core are; cyclic tetramers with rhenium,[129] molecular triangles with platinum,[130] and triple stranded helicates with zinc.[131] Unmodified (R)-(+)-1,1'-binaphthyl-2,2'-diol was used as a ligand, in combination with silver(I), in closley related work by Munakata et al.[132]

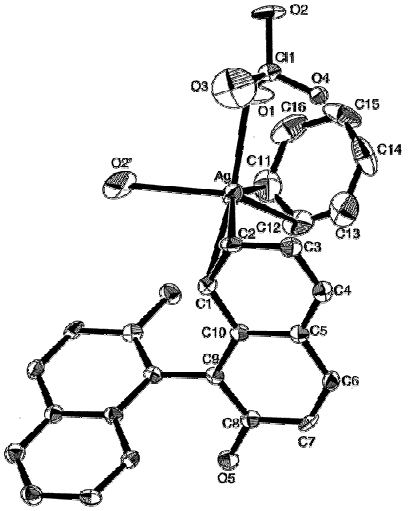
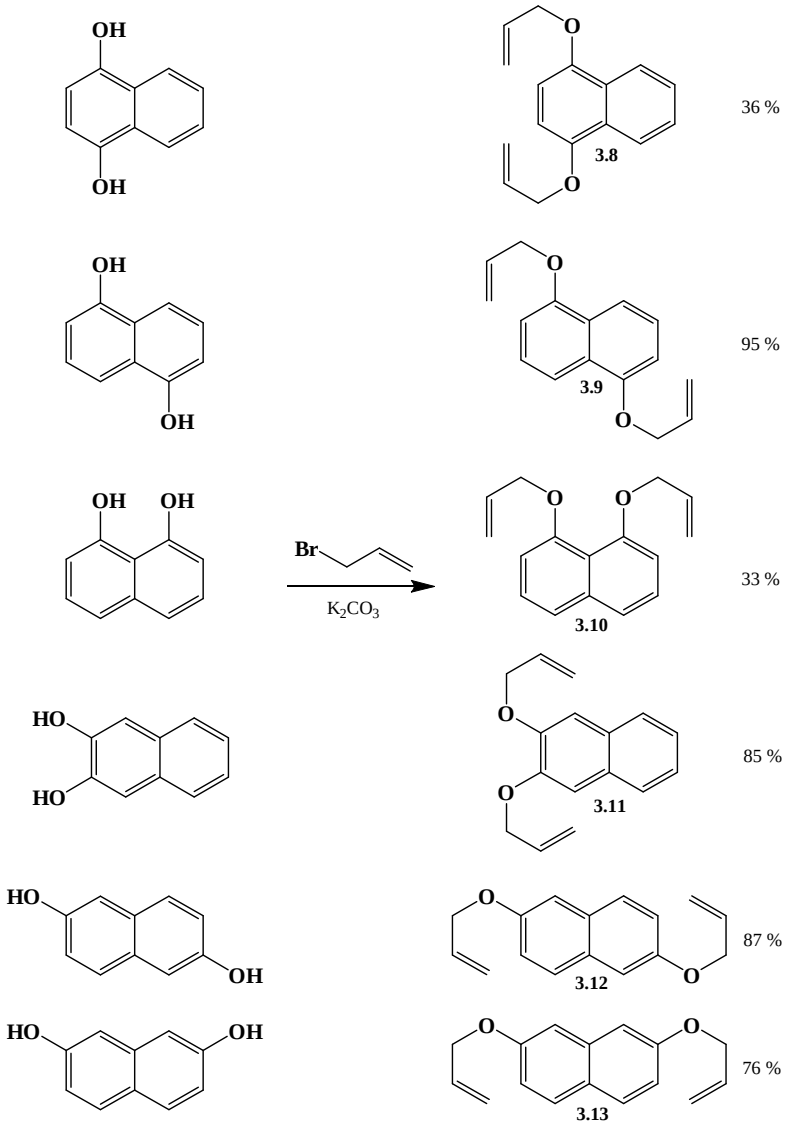


Figure 3.4 *– View of the complex of (R)-(+)-1,1'-binaphthyl-2,2'-diol and silver(I) perchlorate.*[132]

(R)-(+)-1,1'-Binaphthyl-2,2'-diol was combined with silver(I) perchlorate monohydrate in a 1:1 ratio resulting in a three-dimensional porous network. In the resulting complex the free hydroxyl groups are not coordinated to the silver and the silver coordination sphere contains two perchlorate oxygens, one η^2 interaction with the chiral ligand and an η^2 coordinated benzene acting as an auxiliary ligand. The η^2 coordination of (R)-(+)-1,1'-binaphthyl-2,2'-diol to silver occurs at the C7-C8 position, labeled C1-C2 in Figure 3.4. The torsion angle between the two substituted naphthyl rings is 113.7 ° and is larger than in the free ligand which has an angle of 99.2 °.[133]

3.2 Ligand Syntheses

Six symmetrical di(allyloxy)naphthalene isomers were selected; 1,4- (**3.8**), 1,5- (**3.9**), 1,8- (**3.10**), 2,3- (**3.11**), 2,6- (**3.12**) and 2,7-di(allyloxy)naphthalene (**3.13**). The unsymmetrical substitutions 1,2- 1,3- 1,6 and 1,7- were left out of the series as the use of unsymmetrical ligands makes a single product less likely.[111]

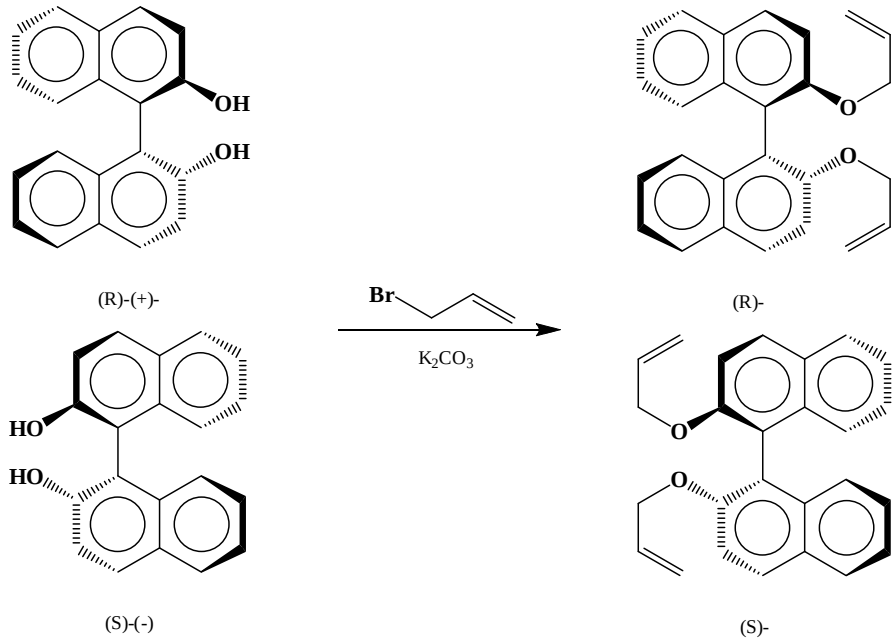


***Scheme 3.1** – Synthesis of the di(allyloxy)naphthalene ligands.*

Ligand **3.8** offers the same geometry and separation as a 1,4- substituted benzene core while **3.9** will give the same 180 ° geometry with the addition of the functional groups being displaced by two bonds. Ligand **3.12** will also give displaced a 180 ° geometry as

in **3.9** but the displacement of the functional groups is now by five bonds. Molecule **3.11** gives the same 60 ° geometry as a 1,2- substituted benzene and **3.13** gives the same 120 ° geometry as 1,3 substitution on a benzene. Ligand **3.13**, while having the same geometry, will have greater separation of the functional groups due to the naphthalene core. Ligand **3.10** will give a displaced 360 ° geometry unavailable in a benzene core.

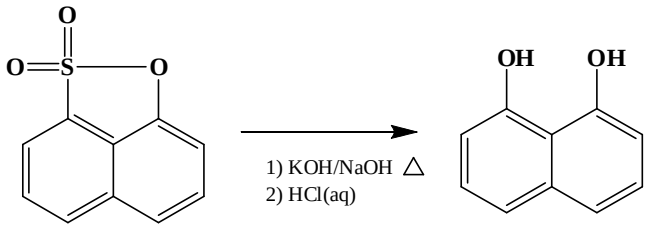
BINOL was incorporated into this ligand series as a precursor to 2,2'-Di(allyloxy)-1,1'-binaphthalene (**3.14**). Both a racemic mix of isomers (**3.14a**) and the enantiomerically pure (R)- (**3.14b**) isomer were used.



***Scheme 3.2** – Synthesis of chiral ligands (**3.14**).*

The synthesis of the ligands in this chapter was achieved via the same methodology established for the preparation of the allyl ether ligand series in chapter two. It consists of selecting the appropriate naphthalenediol precursor and refluxing it with potassium carbonate and allylbromide in acetone for over five hours. This is a one step synthesis with good yields; 25 – 95 %.

All naphthalenediol isomers used in this series, with the exception of 1,8-naphthalenediol, are available commercially. 1,8-Naphthalenediol was made from 1,8-naphthosultone using a literature procedure[134] as shown in Scheme 3.3.



Scheme 3.3 *– Synthetic route to* ***3.10*** *ligand precursor.*

1,4-Di(allyloxy)naphthalene was purified by recrystallisation from petroleum ether. The filtrate from this process was kept and the solvent was allowed to slowly evaporate. The evaporated petroleum ether yielded two different types of crystalline solids; needles and thin plates both of which were analyzed by single crystal X-ray diffraction. The compound that formed thin crystalline plates solved in the orthorhombic space group Pbca and was determined to be ligand **3.8**.

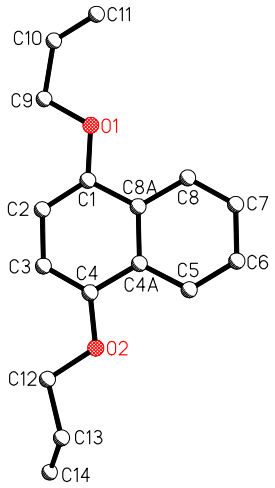
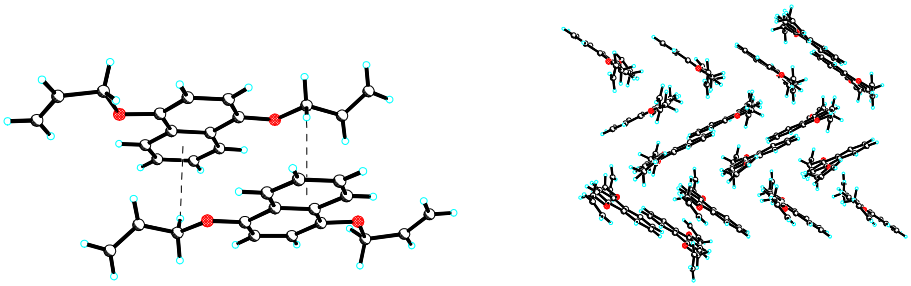


Figure 3.5 *– X-Ray crystal structure of ligand* ***3.8****. View is of the asymmetric unit. Hydrogen atoms have been omitted for clarity.*

Potential symmetry within the ligand is lost due to the asymmetrical solid state conformation of the allyl ether arms. This is reflected in the asymmetric unit, shown in Figure 3.5, as it contains one full molecule of **3.8**. The terminal carbon in the allyl ether at the C1 position twists back towards the oxygen atom where the terminal carbon in the allyl ether arm at the C4 position does not. All atoms in the molecule are approximately planar with the exception of the olefinic carbons; C10, C11, C13 and C14. The out-of-plane torsion angle for C10-C11 is 15.21 ° and 52.95 ° for C13-C14. The plane is calculated using the ten carbon atoms of the naphthalene ring as well as the two ether oxygen atoms.



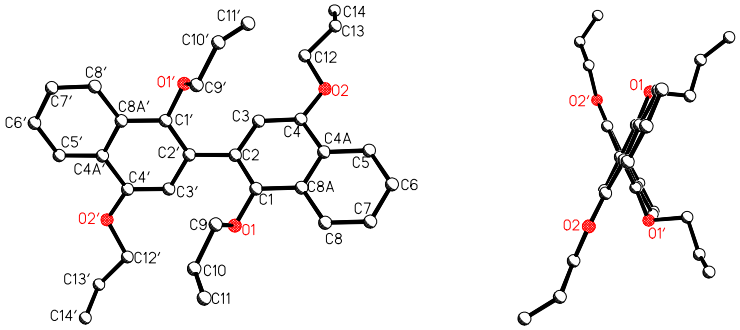
a) ***b)***

Figure 3.6 *– Packing features of* ***3.8****.* ***a)*** *Two molecules of* ***3.8*** *pairing off with offset π-π stacking and C-H/π interactions* ***b)*** *two-dimensional herringbone motif.*

Two molecules of **3.8** pair in offset π-π stacking (3.50 Å) and a C-H/π interaction between a methylene hydrogen and an unsubstituted ring (2.75 Å) as shown in Figure 3.6a. Each molecule within the pair interacts with molecules of neighbouring pairs through further C-H/π interactions, in this case between a hydrogen atom on the C2 position and a substituted ring (2.76 Å) to give a two-dimensional herringbone motif shown in Figure 3.6(b).

The second compound, that formed crystalline needles, solved in the monoclinic space group $P2_1/c$ and was determined to be an allylated coupling product of 1,4-dihydroxynaphthalene (**3.15**) shown in Figure 3.7. Proton NMR was performed on the 1,4-dihydroxynaphthalene starting material which showed an approximate 1:1 mixture of

1,4-dihydroxynaphthalene and 1,4-naphthoquinone with base line impurities. ES-MS of 1,4-dihydroxynaphthalene showed the expected peaks for both 1,4-dihydroxynaphthalene and 1,4-naphthoquinone and also showed the presence of coupling products. It is probable that nucleophilic attack of 1,4-dihydroxynaphthalene on 1,4-naphthoquinone results in conjugate addition giving the 2,2'-Binaphthalene-1,1',4,4'-tetrol precursor which is then allylated.



a) ***b)***

Figure 3.7 *– View of the asymmetric unit of coupling product* ***3.15****. Hydrogen atoms have been omitted for clarity.* ***a)*** *View of the transannular bond* ***b)*** *view looking down the transannular bond.*

As in the single unit **3.8**, potential symmetry within **3.15** is lost due to the asymmetrical solid state conformation of the allyl ether arms. Both allyl ether arms at the C1 positions twist out of the naphthalene ring plane at the O1-C9 and O1'-C9 bond. However the conformation of these two arms is slightly different as the terminal carbon C11 twists towards C8A while C11' twists towards C2'. The allyl ether arms at C4 and C4' do not twist out of the plane at the O2-C12, O2'-C12' bond to the extent of the arms at the C1 positions. The arm at C4 does not twist out at all and has all its atoms except the terminal C14 within the plane of the naphthalene ring. The angle between the planes of the two naphthalene rings is 52.6 °.

Compound **3.15** packs together with C-H/π interactions occurring between the substituted ring of one naphthalene and a methylene hydrogen on C9' from a neighbouring molecule (2.63 Å) and between the unsubstituted ring on the other naphthalene and a methylene

hydrogen on C12 (2.91 Å) as shown in Figure 3.8. These interactions link molecules of **3.15** together to form a three-dimensional network.

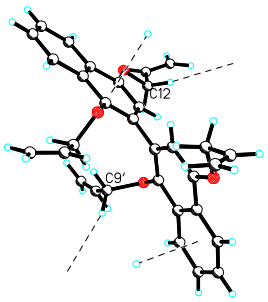
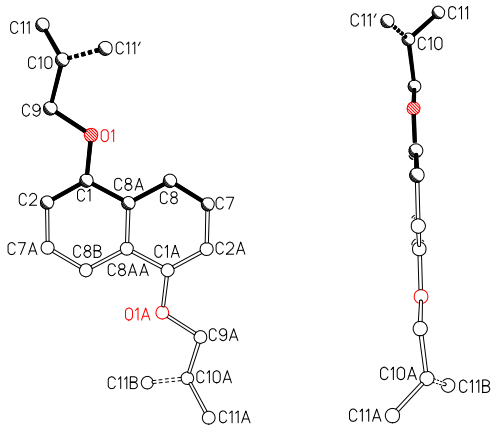


Figure 3.8 *– Four C-H/π interactions found between molecules of* ***3.15****.*

Ligand **3.9** crystallises in the monoclinic space group $P2_1/c$. In the asymmetric unit, (Figure 3.9) there is one half of a molecule of **3.9**, as the molecule lies over a centre of inversion. There is now a symmetry relationship between the configurations of the allyl ether arms; however there is disorder in the terminal olefinic carbon. The terminal carbon has two positions of disorder with each position having 50 % occupancy. This results in three possibilities for the position of the allyl ether arms; both terminal carbons in either the C11 or C11' position or one carbon in the C11 position and the other in the C11' position.



a) ***b)***

Figure 3.9 *- View of the asymmetric unit of* ***3.9****. Hydrogen atoms have been excluded.* ***a)*** *Front view showing the folding of the allyl ether arms* ***b)*** *side view showing the olefinic carbons twisting out of the plane.*

Molecules of **3.9** pack together in a herringbone manner as shown in Figure 3.10.

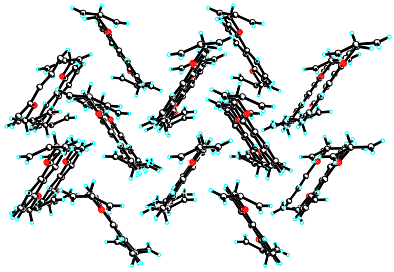
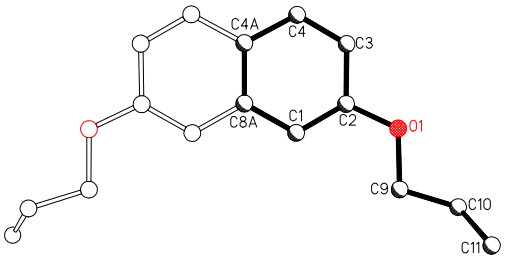


Figure 3.10 *–Herringbone packing motif of* ***3.9****.*

Crystals suitable for X-ray analysis of **3.13** were isolated after slow evaporation from methanol. The structure solved in the orthorhombic space Pbcn. Similar to **3.9**, there is only a half molecule of **3.13** in the asymmetric unit, shown in Figure 3.11(a,b), and in this instance it is related to the other half through a two-fold rotational axis. The molecule is completely planar with the exception of the olefinic bond, C10-C11, which twists out of the plane by 58.3 °.

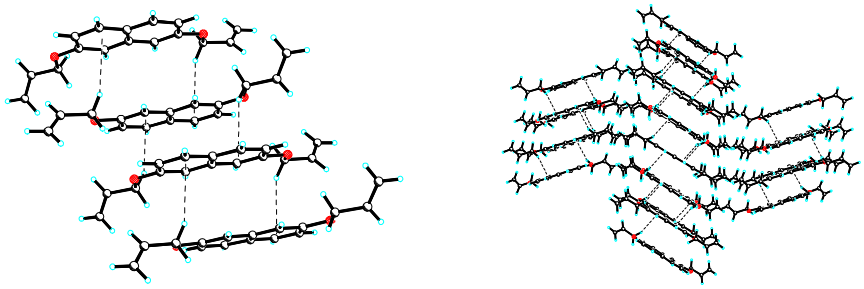


a) ***b)***

Figure 3.11 *– View of the asymmetric unit of* ***3.13****. Hydrogens have been excluded for clarity.* ***a)*** *Front view of* ***3.13*** ***b)*** *side view showing the planarity of the molecule.*

Molecules of **3.13** stack upon each other in an alternating 180 ° fashion creating a one-dimensional tower, as shown in Figure 3.12(a). C-H/π interactions occur within these towers between methylene hydrogen atoms and single rings in the naphthalene core

(2.72 Å). The one-dimensional towers do not interact with each other; however they do stack in a two-dimensional herringbone type manner shown in Figure 3.12(b).



a) ***b)***

Figure 3.12 *– Packing of* ***3.13****.* ***a)*** *One-dimensional towers of* ***3.13*** *with C-H/π interactions* ***b)*** *herringbone packing of the one-dimensional towers.*

Ligand **3.11** crystallises in the monoclinic chiral space group $P2_1$ when dissolved in methanol followed by slow evaporation of the solvent. While the ligand itself is not chiral, the way in which it packs in three dimensions is. The asymmetric unit, shown in Figure 3.13, contains two molecules of **3.11** which have very similar conformations; however their positions and orientation with respect to each other is not related by symmetry. All carbon atoms in each ligand, with the exception of the terminal olefinic carbons, lie approximately on the same plane as the naphthalene ring. The angle between the two naphthalene ring planes approaches right angles at 88.7 ° with edge-to-face π-π stacking between them (2.78 and 2.87 Å). In both molecules of **3.11**, the alkene bond twists out of the plane to the same side with angles of 58.1 °, 42.6 ° 53.5 ° and 55.7 ° for C10-C11, C13-C14, C10'-C11' and C13'-C14' respectively.

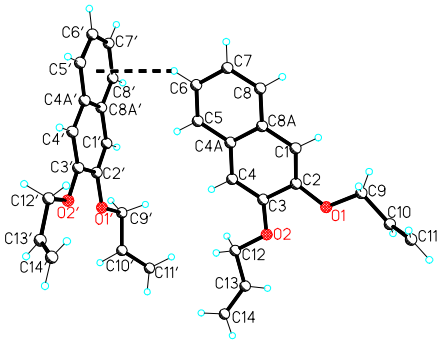
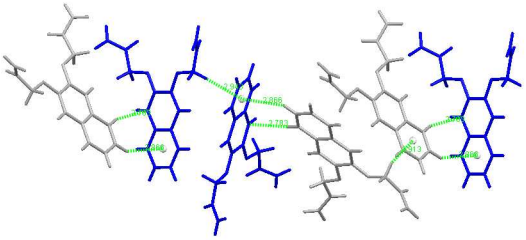
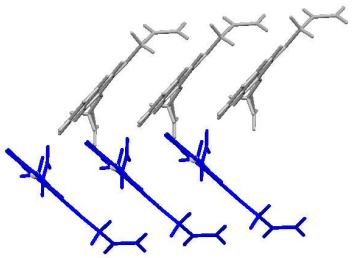


Figure 3.13 *– View of the asymmetric unit with two molecules of* ***3.11****.*

There are two different C-H/π interactions in total and they occur between the unsubstituted ring of one molecule of **3.11** and methylene hydrogen atom on C9 or C9' from a symmetrically equivalent molecule (2.92 and 2.94 Å). This coupled with the edge-to-face π-π stacking previously mentioned links molecules of **3.11** in one dimension, as seen in Figure 3.14(a). Molecules of **3.11** interact in the second dimension through offset π-π stacking (3.52 Å) between symmetry equivalent molecules, as seen in Figure 3.14(b).



a)



b)

Figure 3.14 *– View of the packing of* ***3.11*** *molecules.* ***a)*** *View of the weak CH/π interactions* ***b)*** *view of offset π-π stacking.*

Ligand **3.12** was recrystallised from petroleum ether and the crystal structure was solved in the monoclinic space group $P2_1/c$. There are two symmetrically independent half molecules within the asymmetric unit, shown in Figure 3.15, where each half molecule lies over a centre of inversion. The two ligands are not symmetrically equivalent due to the different solid state conformation of the allyl ether substituents.

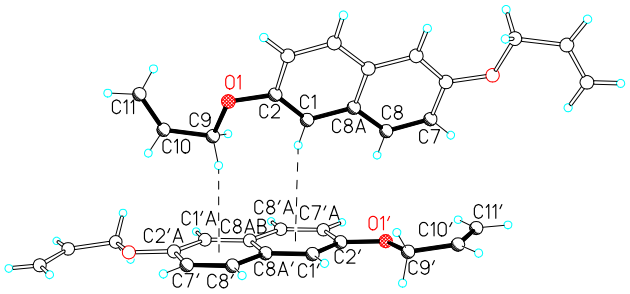
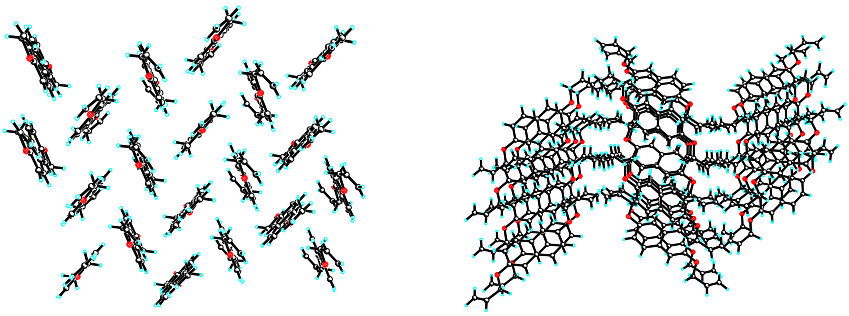


Figure 3.15 *– View of the asymmetric unit of ligand* ***3.12****.*

The molecule at the top of Figure 3.15 has the allyl ether arms twisting out of the plane of the naphthalene ring at the C9-C10 bond. This twisting accommodates a C-H/π interaction between the centroid of C1'A, C2'A, C7', C8', C8A', C8AB and one of the methylene hydrogens on C9 (2.69 Å). The angle between the double bond and the plane of the naphthalene ring is 18.5 °. The molecule at the bottom of Figure 3.15 has all its atoms lying in the same plane with the exception of the terminal carbon C11'. The C10'-C11' bond is out of the plane by a very slight angle of 6.5 °. The angle between planes of the two different naphthalene rings is 62.7 °.



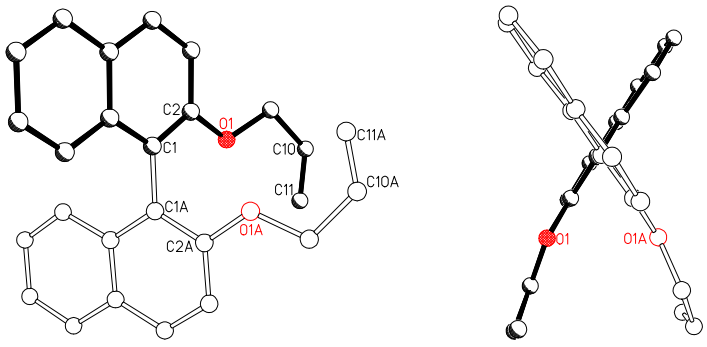
a) ***b)***

Figure 3.16 – a) *Herringbone packing in* ***3.12*** ***b)*** *view of allyl ether arms pointing towards each other.*

A two-dimensional network of **3.12** is made up of interactions as shown in Figure 3.15, as well as additional edge-to-face π-π stacking giving an overall herringbone type packing. The allyl ether arms of **3.12** lie above and below the plane of these sheets and

they fit together into the third dimension at 90 ° angles to each other with no interactions in between.

Crystals of **3.14b** suitable for X-ray crystallography were obtained from the reaction mixture. Single crystal X-ray analysis was performed and the structure solved in the chiral tetragonal space group $I4_1$. This indicates that the compound is a single enantiomer although it could not be said which, but in all likelihood it is the R- enantiomer.



a) ***b)***

Figure 3.17 *– View of the asymmetric unit of* ***3.14b****. Hydrogen atoms have been omitted for clarity.* ***a)*** *View of the transannular bond* ***b)*** *looking down the transannular bond.*

The asymmetric unit, shown in Figure 3.17, contains a half molecule of **3.14b** with the second half of the molecule related by a two-fold rotation axis. The allyl ether substituents twists out of the plane of the naphthalene ring at the O1-C9 bond with the double bond angled at 11.0 °. The torsion angle between the two naphthalene rings is 65.5 ° which is smaller than the angle found in Munakata's (R)-(+)-1,1'-binaphthyl-2,2'-diol silver(I) complex (113.7 °)[132] and in the free (R)-(+)-1,1'-binaphthyl-2,2'-diol (99.2 °) and its racemic form (88.6 °).[133]

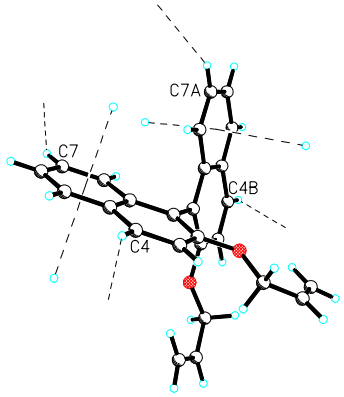


Figure 3.18 *– View of C-H/π interactions in* ***3.14b****.*

There are two different C-H/π interactions occurring within the solid state and a total of eight in any one molecule of **3.14b**. Each C-H/π interaction occurs between the unsubstitued ring in the naphthalene and either a hydrogen on C4 (2.66 Å) or C7 (2.97 Å). Each unsubstitued ring within **3.14b** has two C-H/π interactions, one above and one below the plane of the ring as seen in Figure 3.18. These interactions link molecules of **3.14b** together in a three-dimensional network.

3.3 Complexes of 1,4-Di(allyloxy)naphthalene

With silver(I) perchlorate (**3.16**)

Ligand **3.8**, dissolved in chloroform, was mixed with an acetone solution of silver(I) perchlorate. Diethyl ether was allowed to diffuse into the combined solution and upon evaporation crystals suitable for X-ray analysis formed. The structure solved in the monoclinic space group Cc. The asymmetric unit reveals silver atoms disordered over three positions, where the dominant position, Ag1, has 90 % occupancy. Figure 3.19 shows the contents of the asymmetric unit which contains one silver atom, one organic ligand and one coordinating perchlorate anion.

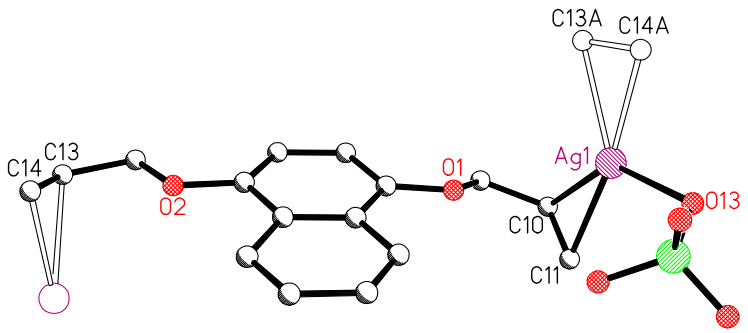


Figure 3.19 *– View of the asymmetric unit of* ***3.16*** *showing only the major position of silver occupancy. Hydrogen atoms have been excluded for clarity. Selected bond lengths (Å) and angles (°): Ag1-C10 2.38 (1), Ag1-C11 2.34(1), Ag1-C13A 2.47(1), Ag1-C14A 2.31(1), Ag1-O13 2.37(1), C10,C11-Ag1-C13A,C14A 132.95(5), C13A,C14A-Ag1-O13 104.38(4), C10,C11-Ag1-O13 122.66(5).*

The structure consists of one ligand **3.8** bridging two silver atoms through the alkenes in both allyl ether arms. As in the free ligand, **3.8**, this complex does not have its allyl ether arms in a symmetrical conformation. Each silver atom has a distorted trigonal planar geometry and is bonded to two alkenes, from different ligands, and to one oxygen atom from the perchlorate anion.

The complex extends into a one-dimensional polymer and continuously folds back upon itself, shown in Figure 3.22(a), similar to the benzene analogue, **2.13**. Also like **2.13** the aromatic rings are within appropriate distances, 3.49 to 3.52Å, for π-π stacking interactions to occur. The aromatic rings in this case are staggered relative to one another and do not stack directly above and below each other. The Ag···Ag separation, when measured across the bridging ligand **3.8**, is 11.22 Å. This too is comparable to the analogous benzene complex **2.13** which has a distance of 11.35 Å.

Within the crystal packing individual polymer strands align with neighbouring ones through multiple weak interactions between perchlorate oxygen atoms of one strand and

silver atoms in another. However the structure is not as simple as this when the disorder of the silver is taken into account. The second position of silver, Ag1', shown in Figure 3.20, has 5 % occupancy and is shifted toward the naphthalene ring compared to Ag1. This allows for the silver to bond to the allyl ether oxygen, while still remaining bonded to the terminal alkene. This is a previously unseen mode of bonding. As the silver has moved closer to the naphthalene ring, it has, in turn, moved away from the perchlorate so only weak interactions (Ag1'-O13 2.77 Å) now occur between the oxygen on the perchlorate and the silver atom.

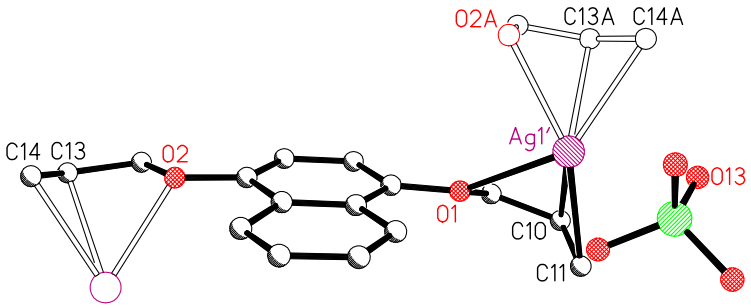


Figure 3.20 *– View of the asymmetric unit of* ***3.16*** *showing the first, of two, minor occupancies of silver. Selected bond lengths (Å) and angles (°): Ag1'-O1 2.40(3), Ag1'-C11 2.50(3), Ag1'-C10 2.53(4), Ag1'-O2A 2.53(3), Ag1'-C13A 2.51(4), Ag1'-C14A 2.60(3), O1-Ag1'-O2A 89.8(9), C13A,C14A-Ag1-C10,C11 133.0(1), C13A,C14A-Ag1-O1 135.3(2), C13A,C14A-Ag1-O2A 64.40(9), C10,C11-Ag1-O1 68.74(9), C10,C11-Ag1-O2A 146.4(2).*

If the complex had been comprised of silver solely in the Ag1' position, it would form a one-dimensional polymer, similar to one comprised solely of Ag1, but with no interactions between polymer strands as shown in Figure 3.22(b).

The third position of silver, Ag1”, fills the remaining 5% of occupancy and is shown in Figure 3.21. The new position is further away from the naphthalene ring compared to Ag1. This shift allows a second oxygen on the perchlorate to bond to the silver and enables the perchlorate to bridge the silver atoms. As a result of shifting away from the naphthalene ring, the silver atom is only bound to the terminal carbon, C14, on one of the allyl ether arms and is no longer bound at all to the second alkene, C10,C11, in the other arm. As a consequence of this, the silver is no longer bridged by ligand **3.8** and polymer propagation is now through bridging perchlorate anions. The bond distance between the terminal alkene carbon, C14, and silver is much shorter than when both carbons are coordinated.

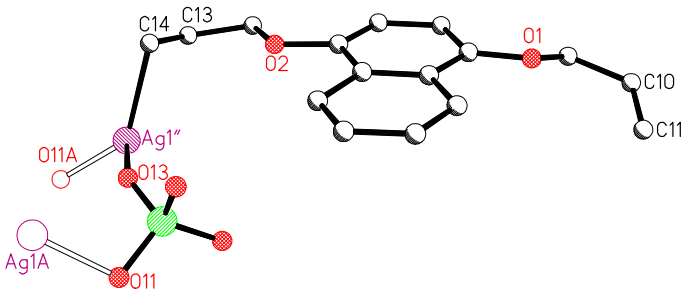
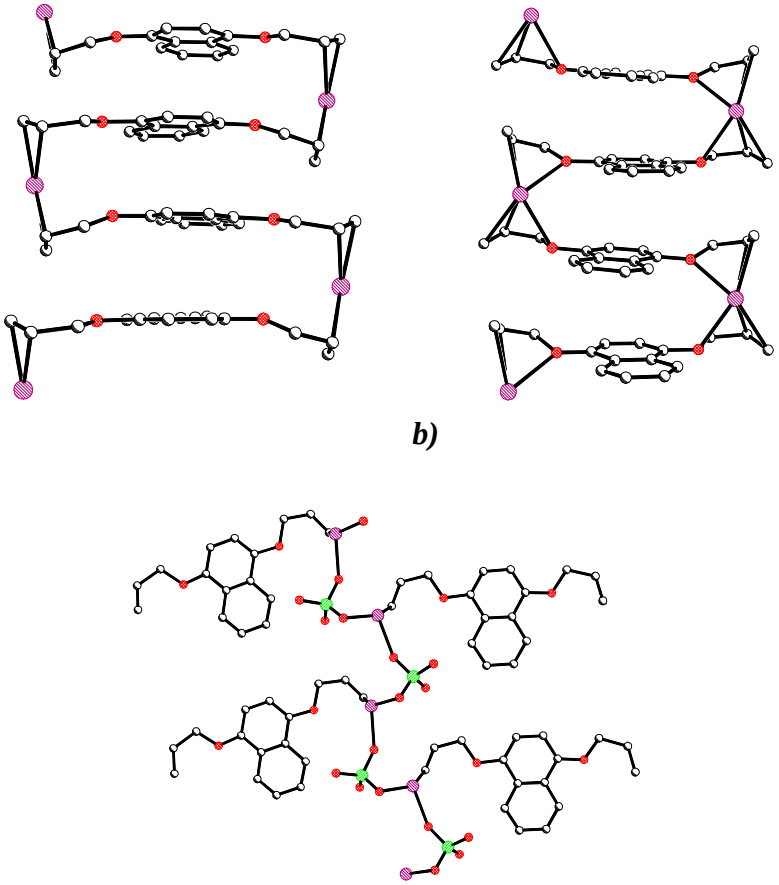


Figure 3.21 *– View of the asymmetric unit of* ***3.16*** *showing the second of two minor occupancies of silver. Selected bond lengths (Å) and angles (°): Ag1"-O13 2.26(4), Ag1"-O11A 1.93(3), Ag1"-C14 2.29(3), O11A-Ag1"-O13 106.0(2), O11A-Ag1"-C14 136.8(2), O13-Ag1"-C14 91.8(1).*

If **3.16** had been comprised of silver solely in the Ag1” position it would now form a one-dimensional polymer that propagates perpendicular to one solely comprised of Ag1. The silver is now bridged solely by perchlorate counter anions with ligand **3.8** coordinated, in a monodentate fashion, to the silver-perchlorate backbone as shown in Figure 3.22(c).



a) ***b)*** ***c)***

Figure 3.22 *– View of different polymers of* ***3.16****.* ***a)*** *Comprised of Ag1* ***b)*** *comprised of Ag1' **c)** comprised of Ag1".*

3.4 Complexes of 1,5-Di(allyloxy)naphthalene

With silver(I) triflate (**3.17**)

A solution of ligand **3.9** in chloroform was combined with silver(I) triflate in acetone. Diethyl ether was diffused into the mixture and slow evaporation of the solvents was allowed to take place. This yielded crystals suitable for X-ray crystallography and the structure solved in the triclinic space group P-1. The asymmetric unit consists of one silver atom, one coordinate triflate counter anion and one half of the ligand **3.9** as shown in Figure 3.23.

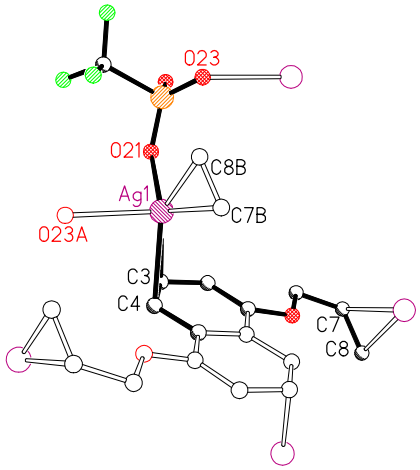


Figure 3.23 *– The asymmetric unit of* ***3.17****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O21 2.341(1), Ag1-O23A 2.527(1), Ag1-C3 2.591(2), Ag1-C4 2.461(2), Ag1-C3,C4 2.429(2), Ag1-C7B 2.468(2), Ag1-C8B 2.360(2), Ag1-C7B,C8B 2.319(2), O21-Ag1-O23A 100.03(4), C3,C4-Ag1-C7B,C8B 132.72(6), O23A-Ag1-C7B,C8B 101.28(6), O21-Ag1-C7B,C8B 117.13(5), O23A-Ag1-C3,C4 95.82(5), O21-Ag1-C3,C4 102.49(5).*

The organic ligand **3.9** lies on a crystallographic centre of inversion and both allyl ether arms have symmetry related solid state conformations. Each ligand is coordinated to four silver atoms, two through the alkenes on the allyl ether arms and two through η^2 coordination to the naphthalene ring.

The silver is coordinated to the naphthalene ring in the C3,C4 and the C7,C8 positions. Both of these positions are where silver is predicted to coordinate.[122] Coordination at these positions slightly lengthens the bond between the two carbons; C3-C4 1.391(2) Å, C7-C8 1.391(2) Å, compared to the free ligand (C3-C4 1.373(4), C7-C8 1.364(3)). The bonds on either side of the C3,C4 position; C2-C3 1.427(2) Å, C4-C4A 1.436(2) Å, are also lengthened when compared to the free ligand (C2-C3 1.414(3) Å, C4-C4A 1.417(3)

Å), but not in the C7,C8 position. Other bond length comparisons around the naphthalene ring are within experimental error of each other.

Each silver atom in **3.17** is four coordinate with two triflate oxygen atoms, one alkene and one η^2 arene in its coordination sphere. Silver atoms have a calculated τ_4 value of 0.78 indicating a distorted trigonal pyramidal geometry. A single silver atom is doubly bridged by the triflate anion and ligand **3.9** to two other silver atoms and additionally bridged to a further two silver atoms by ligand **3.9**. The distance between the centroid of the two carbons in the η^2 interaction and the silver atom is longer than those between the olefinic carbon centroid and the silver.

The Ag···Ag distance measured across ligand**3.9**, from Ag1B to Ag1H, is 10.76 Å. This is slightly shorter compared to the 11.22 Å Ag···Agdistance across **3.8** in complex **3.16**. Other Ag···Ag distances include: 7.38 Å between Ag1B and Ag1D, 6.91 Å between Ag1D and Ag1G and 5.22 Å between Ag1D and Ag1H.

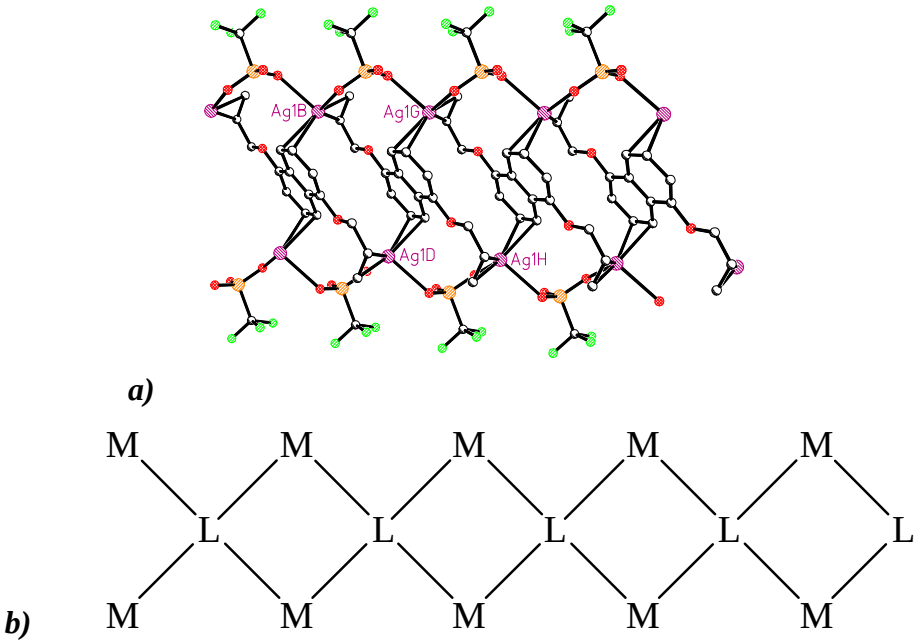


Figure 3.24 *– View of the one-dimensional polymer* ***3.17****.* ***a)*** *View of a section of the one-dimensional polymer* ***b)*** *a simplified representation of the necklace polymer, where M = Ag*$^+$*, L = ligand* ***3.9****.*

The overall structure is a complicated one-dimensional polymer, shown in Figure 3.24(a), which can be described as a necklace polymer. Ligand **3.9** acts as a four connecting node in conjunction with the silver(I) acting as a two connecting node, as shown in Figure 3.24(b). The triflate anions cap the third and fourth coordination sites of the silver atoms.

The one-dimensional polymer chains interact with each other through weak hydrogen bonding between hydrogen atoms on ligand **3.9** and fluorine atoms on the triflate. The close packing of the crystal structure forces the close proximity of triflate fluorine atoms with the closest distance between fluorine atoms on adjacent triflates being 2.796(2) Å. This arises as a result of steric crowding and crystal packing rather than attractive interactions.[135-138]

3.5 Complexes of 1,8-Di(allyloxy)naphthalene

With silver(I) triflate (**3.18**)

Ligand **3.10** was combined with silver(I) triflate resulting in the formation of crystals suitable for X-ray crystallography. The structure solved in the monoclinic space group $P2_1/c$. The asymmetric unit, shown in Figure 3.25, consists of one silver atom, one non-coordinating triflate anion and one molecule of **3.10** with an overall structure of a [2+2] macrocycle.

Each macrocycle contains two silver atoms and two molecules of **3.10**. The silver atoms have approximate trigonal planar geometry and are coordinated to two alkenes from one ligand and one η^2 arene from the second ligand. As in **3.17**, the silver has attached to the naphthalene ring in one of the predicted positions.[122] Also similar to the previous complex, **3.17**, the distance between the centroid of the two carbons in the η^2 interaction and the silver atom in **3.18** is marginally longer than the distance between the olefinic carbon centroid and silver. The [2+2] macrocycle is formed by ligand **3.10** coordinating to one silver atom through chelation of the alkenes from both allyl ether arms and bridging to the second silver atom through an η^2 coordination at the C5,C6 position on

the naphthalene ring. This is the only example of the chelation of allyl ether arms in this thesis. The Ag···Ag separation across ligand**3.10** is 7.34 Å.

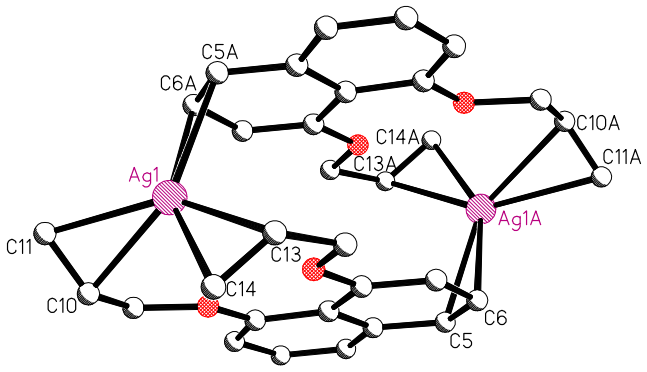


Figure 3.25 *– View of discrete [2+2] macrocyclic* ***3.18****. Hydrogen atoms have been excluded for clarity. Selected bond lengths (Å) and angles (°): Ag1-C5A 2.472(3), Ag1-C6A 2.581(3), Ag1-C5A,C6A 2.433(3), Ag1-C10 2.503(3), Ag1-C11 2.510(3), Ag1-C10,C11 2.416(3), Ag1-C13 2.481(3), Ag1-C14 2.425(3), Ag1-C13,C14 2.360(3), C5A,C6A-Ag1-C10,C11 111.9(1), C5A,C6A-Ag1-C13,C14 126.9(1), C10,C11-Ag1-C13,C14 119.9(1).*

Within the crystal packing the discrete units stack with other units through shifted π-π stacking interactions and the non-coordinated triflate anion weakly hydrogen bonds through its oxygen atoms with hydrogen atoms in ligand **3.10**.

With silver perchlorate (3.19)

Under the same conditions as for the formation of **3.18**, silver(I) perchlorate was reacted with ligand **3.10** also yielding crystals suitable for X-ray analysis. The structure solved in the triclinic space group P-1. The asymmetric unit contains one disordered silver atom, one ligand **3.10**, one half of a water molecule and one disordered non-coordinating perchlorate anion. The overall structure is a [2+2] macrocycle very similar to **3.18**.

The disorder in the silver is over two positions, with each position having 50 % occupancy. Not enough information is available to determine whether each macrocycle contains two silver atoms in each position of disorder, or whether the macrocycles contain silver atoms exclusively occupying one position or the other. It is likely that all three possibilities are occurring. Figure 3.26 shows the [2+2] macrocycle with two silver atoms, one occupying each of the positions.

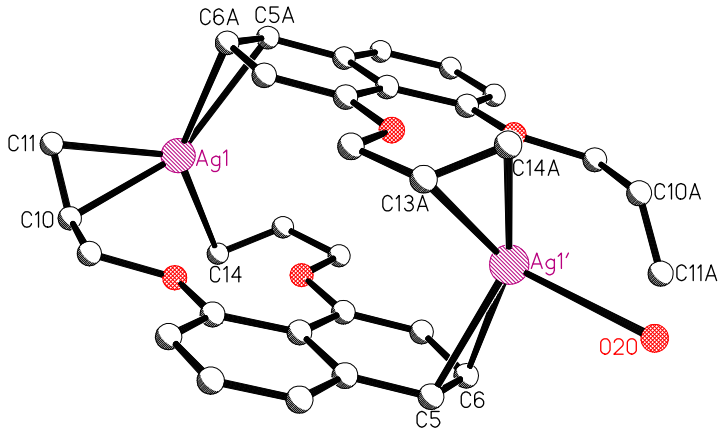


Figure 3.26 *– View of the discrete [2+2] macrocycle* ***3.19*** *with both occupancies of silver displayed. Hydrogen atoms and counter anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C5A 2.600(4), Ag1-C6A 2.436(4), Ag1 C5A,C6A 2.425 (4), Ag1-C10 2.230(6), Ag1-C11 2.220(7), Ag1-C10,C11 2.125(7), Ag1-C14 2.598(5), Ag1'-C5 2.429(4), Ag'-C6 2.596(4), Ag1'-C5,C6 2.420(4), Ag'-C13A 2.264(6), Ag1'-C14A 2.224(5), Ag1'-C13,C14 2.146(6), Ag1'-O20 2.597(8), C5A,C6A-Ag1-C14 128.9(2), C5A,C6A-Ag1-C10,C11 123.6(2), C10,C11-Ag1-C14 107.3(2), O20-Ag1'-C5,C6 101.2(2), O20-Ag1'-C13A,C14A 102.7(2), C5,C6-Ag1'-C13A,C14A 137.8(2).*

In both positions of disorder silver atoms are three coordinate; Ag1 has close to trigonal planar geometry and Ag1' has a more T shaped geometry. Ag1 has one alkene (C10,C11) very closely bound, an η^2 interaction with the naphthalene ring at the C5,C6 position and

a weaker interaction with one carbon from the second alkene. The second position of silver, Ag1', has an η^2 interaction with the naphthalene ring at the C5,C6 position and one of the alkenes closely bound (C13,C14). Ligand **3.10** is no longer chelating to the silver atoms in this position as the second alkene is non-coordinating. The oxygen of the water molecule, O20, is shown interacting with Ag1' in Figure 3.26 but it can also weakly interact with Ag1 (Ag1-O20 2.61 Å), however it only has 50 % occupancy and may only be associated with Ag1'. The Ag···Ag separation in this macrocycle is slightly shorter than in **3.18** with an average distance of 7.02 Å. As in **3.18**, the silver has coordinated to the naphthalene ring in the C5,C6 position.

The macrocycles pack in a manner much the same as **3.18**, where the discrete units stack above and below each other with π-π stacking interactions between the naphthalene rings of adjacent units. The perchlorate anion is involved in weak hydrogen bonds betweens its oxygen atoms and hydrogen atoms on ligand **3.10**.

3.8 Complexes of 2,3-Di(allyloxy)naphthalene

With silver(I) hexafluorophosphate (**3.20**)

Ligand **3.11**, dissolved in chloroform, was mixed with an acetone solution of silver(I) hexafluorophosphate. Diethyl ether was allowed to diffuse into the combined solution and upon evaporation, crystals suitable for X-ray analysis formed. The structure solved in the triclinic space group P-1. The asymmetric unit of **3.20** consists of one silver atom disordered over two positions, one molecule of **3.11**, and a highly disordered, non-coordinating hexafluorophosphate counter anion. Figure 3.27 shows the contents of the unit cell including both positions of the silver atom.

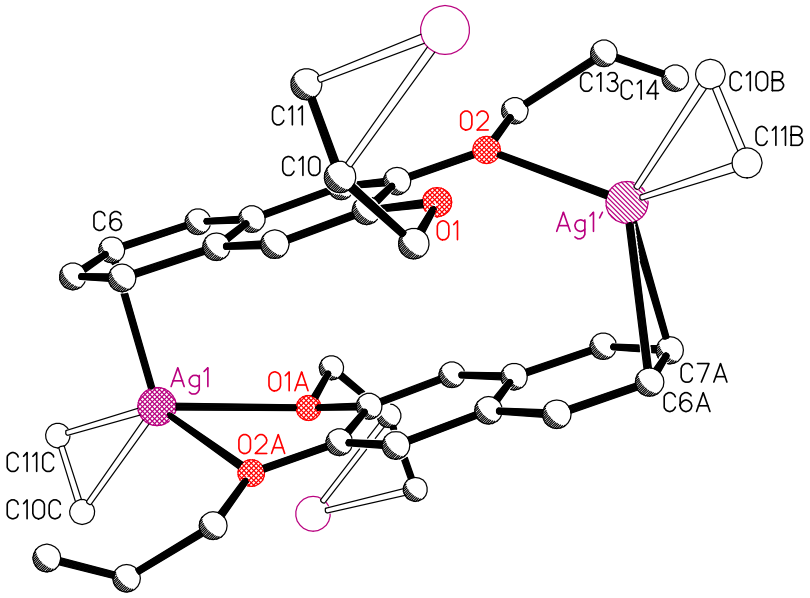


Figure 3.27 *- View of the unit cell contents of* ***3.20****, showing both positions of occupancies of silver. The hydrogen atoms, counter anion and further disorder have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O1A 2.425(5), Ag1-O2A 2.482(4), Ag1-C10C 2.407(6), Ag1-C11C 2.269(6), Ag1-C10C,C11C 2.242(6), Ag1-C6 2.562(8), Ag1'-O2 2.323(4), Ag1'-C6A 2.580(9), Ag1'-C7A 2.409(7), Ag1'-C10B 2.567(7), Ag1'-C11B 2.518(7), Ag1'-C10B,C11B 2.454(7), O1A-Ag1-O2A 62.8(2), O1A-Ag1-C10C,C11C 121.6(3), O2A-Ag1-C10C,C11C 127.3(2), O1A-Ag1-C6 107.8(2), O2A-Ag1-C6 114.1(2), C6A-Ag1'-C10C,C11C 113.0(2), O2-Ag1'-C6A,C7A 117.8(2), O2-Ag1'-C10B,C11B 109.1(2), C6A,C7A-Ag1'-C10B,C11B 113.8(2).*

In this structure the silver is disordered over two positions, with each position having 50 % occupancy. The silver is pulled in two opposing directions, where one direction favours the chelation of the oxygen atoms in the allyl ether arms and the other favours the η^2 coordination of the naphthalene ring. In the first position, Ag1, the silver is four coordinate with a calculate τ_4 value of 0.79 indicating a distorted trigonal pyramidal geometry. It coordinates through two chelating oxygen atoms from the allyl ether arms,

as well as one alkene from an allyl ether arm and one carbon from the naphthalene ring. This position favours the chelation of the allyl ether oxygen atoms at the expense of the η^2 coordination to the naphthalene ring. In the second position, Ag1', the silver is three coordinate with approximate trigonal planar geometry. It coordinates to one oxygen atom and one alkene from an allyl ether arm as well as the naphthalene ring via an η^2 fashion. This position of the silver atoms favours the η^2 coordination to the naphthalene ring at the expense of the chelation of the oxygen atoms from the allyl ether arms.

Ligand **3.11** is coordinated to three silver atoms and bridges them in three different ways. Firstly through η^2 or η^1 coordination of the naphthalene ring to the silver atom and bridging to another silver atom through either the coordination of one, or the chelation of two, of the oxygens in the allyl ether arms. The second mode of bridging is through η^2 or η^1 coordination of the naphthalene ring to silver then connecting to another silver atom through the coordination of an alkene on one of the allyl ether arms. The last type of bridging is through the coordination of one, or the chelation of two, of the oxygen atoms in the allyl ether arms to silver and then bridging to another silver atom through an alkene on one of the allyl ether arms. One of the alkenes in an allyl ether arm is non-coordinating and is disordered over two positions.

Unlike the previous two examples of η^2 coordination of a naphthalene ring this structure contains coordination to the aromatic system at the C6,C7 position, one of the longer bonds. As a result of the coordination of a silver atom the bond length of C6-C7 (1.35(1) Å) is significantly shorter than in the free ligand, C6-C7 (1.417(5) Å). Conversely, the bonds connecting the adjacent carbons are slightly longer, C5-C6 1.41(1) Å, C7-C8 1.40(1) Å, compared to the free ligand, C5-C6 1.376(4) Å, C7-C8 1.383(5) Å. This suggests that the electron density is being drawn from the adjacent bonds (C5-C6 and C7-C8) and localised in the C6,C7 bond. Other bond distances around the naphthalene ring are within experimental error of each other with the exceptions of C2-C3 1.42(1) Å and C8A-C4A 1.40(1) Å, which are both shorter compared to the free ligand.

The Ag···Ag separation across**3.11**, Ag1B···Ag1A in Figure 3.28, in**3.20** is an average of 8.32 Å. This is longer compared to both **3.18** (7.34 Å) and **3.19** (7.02 Å) which is to be expected as the ligand in **3.20** is bridging over the longer axis of the naphthalene ring, rather than the shorter axis as in **3.18** and **3.19**. Other Ag···Ag distances include 10.17 Å between Ag1B and Ag1D and 5.28 Å between Ag1A and Ag1D.

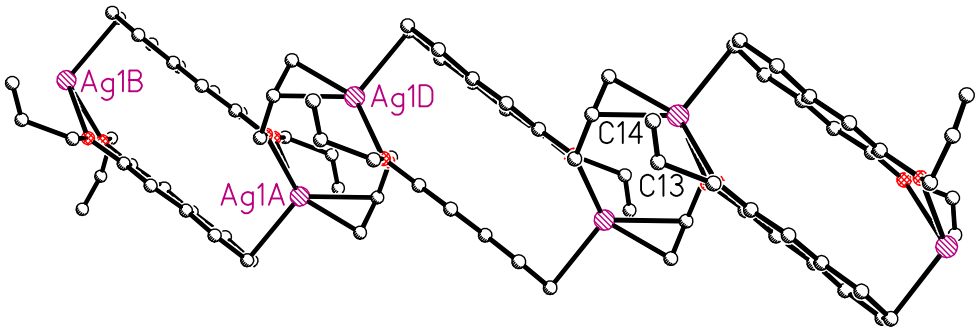


Figure 3.28 *- Section of the one-dimensional polymer* ***3.20*** *showing non-coordinating olefinic carbons C13 and C14. Only one of the occupancies of the silver atom is displayed.*

The complex is a one-dimensional polymer with staggered π-π interactions between naphthalene rings, within and between polymer strands. Within the crystal packing there are also numerous weak hydrogen bonding interactions between the hydrogen atoms in ligand **3.20** and fluorine atoms on the hexafluorophosphate counter anion.

3.6 Complexes of 2,6-Di(allyloxy)naphthalene

With silver(I) tetrafluoroborate (**3.21**)

Ligand **3.12** was dissolved in chloroform and the resulting solution added to solid silver(I) tetrafluoroborate. The chloroform was then allowed to evaporate yielding crystals suitable for single crystal X-ray analysis. The structure was solved in the monoclinic space group $P2_1/c$. However, while the solution makes chemical sense, the

R(int)[‡], R(sigma)[§] and R_1[**] values are poor, and it is likely due to twining. A second crystal was analysed and similar problems occurred. The asymmetric unit, shown in Figure 3.29, contains two crystallographically independent half ligands, one silver atom and one non-coordinating tetrafluoroborate anion.

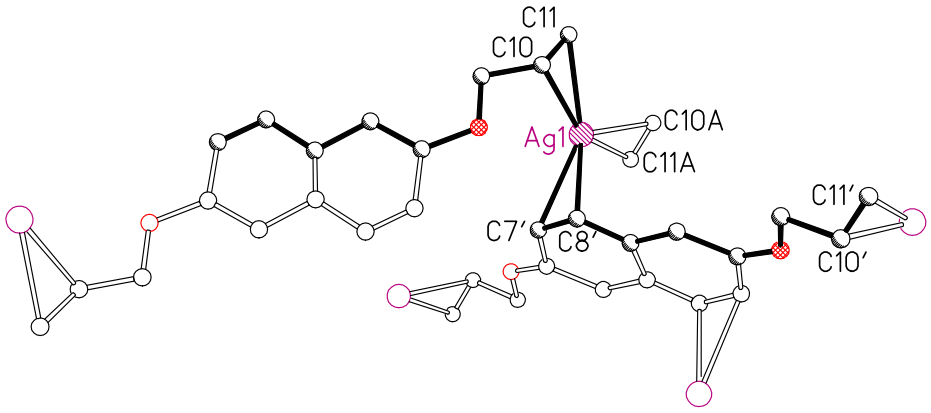


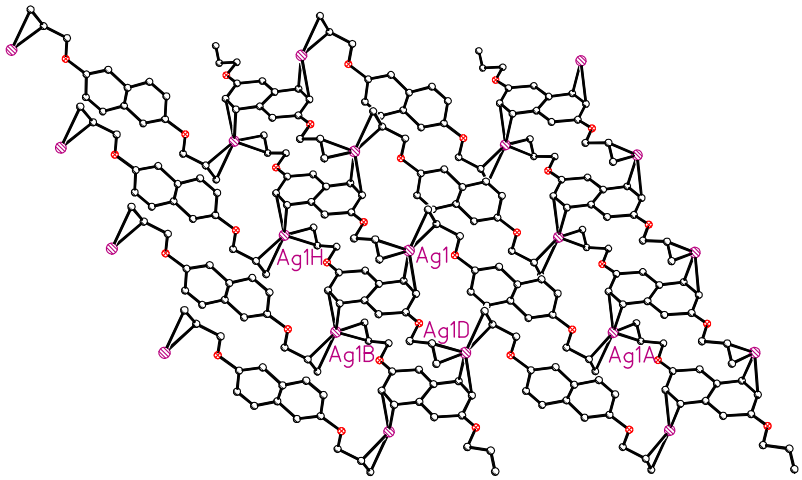
Figure 3.29 *– View of the asymmetric unit of* ***3.21****. Hydrogen atoms and counter anions are omitted for clarity. Bond lengths and angles are not listed due to the poor refinement.*

In this structure, the silver atoms are three coordinate with approximate trigonal planar geometry. Each silver atom has two alkenes and one η^2 naphthalene coordinated. As in the free ligand, the two molecules of **3.12** lie on crystallographic centres of inversion.

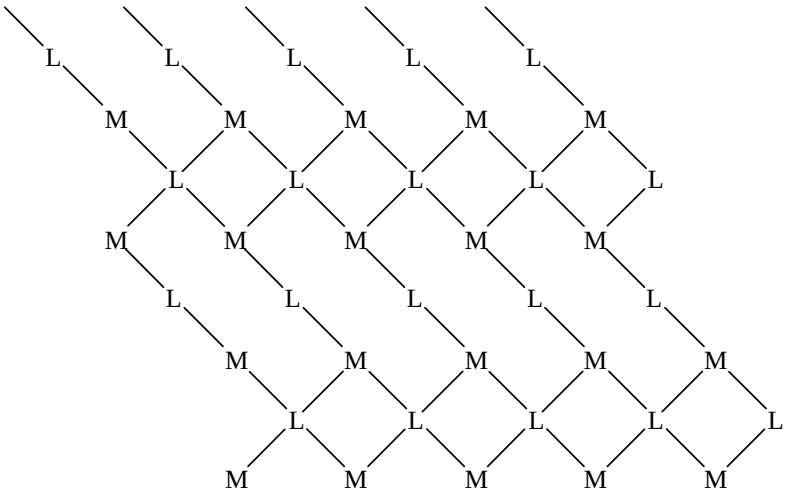
Ligand **3.12** bridges silver atoms in two different ways. In the first, the ligand simply bridges two silver atoms by coordination of both alkenes in the allyl ether arms. In the second, it bridges four silver atoms in a remarkably similar manner to ligand **3.9** in complex **3.17**. The ligand is tetradentate and bridges two silver atoms through the alkenes in the allyl ether arms, as they did above, as well as bridging a further two silver atoms through η^2 coordination of the naphthalene ring at the C3,C4 and C7,C8 positions.

[‡] R(int) is a measure of the agreement between observed symmetry-equivalent data.
[§] R(sigma) is a measure of the variance in the intensities of reflections.
[**] R_1 is a measure of how well the calculated diffraction pattern of the model fits the observed one.

Approximate distances between silver atoms measured the two allyl ether arms of ligand **3.12**, Ag1···Ag1A and Ag1D···Ag1H in Figure 3.30(a), are 13.8 Å and 13.5 Å respectively. These are the longest Ag···Ag separations achieved by the linear allyl ether ligands; **2.9**, **3.8**, **3.9** and **3.12**. The approximate Ag···Ag separation between Ag1 and Ag1B is 7.10 Å which is comparable to the value of 7.38 Å occurring between similarly bridged silver atoms in **3.17**.



a)



b)

Figure 3.30 – a) *View of the two-dimensional nature of polymer* ***3.21 b)*** *schematic representation of the two-dimensional network.*

The structure can be considered a one-dimensional necklace polymer, similar to **3.17**, that are further bridged by further molecules of **3.12** in a bidentate manner to give an overall two-dimensional sheet. There are staggered π-π stacking interactions between ligands within a polymer sheet and the two-dimensional sheets stack upon each other in a ABAB manner with weak Ag···F-BF_3 and CH···F interactions between them.

3.7 Complexes of 2,7-Di(allyloxy)naphthalene

With silver(I) triflate (**3.22**)

Ligand **3.13** was reacted with silver(I) triflate in an acetone/chloroform solution with diethyl ether diffusion. Slow evaporation of the solvents yielded a crystalline product suitable for X-ray analysis. The structure solved in the triclinic space group P-1. Figure 3.31 shows the asymmetric unit which contains; one silver atom, one ligand **3.13** and a coordinated triflate anion.

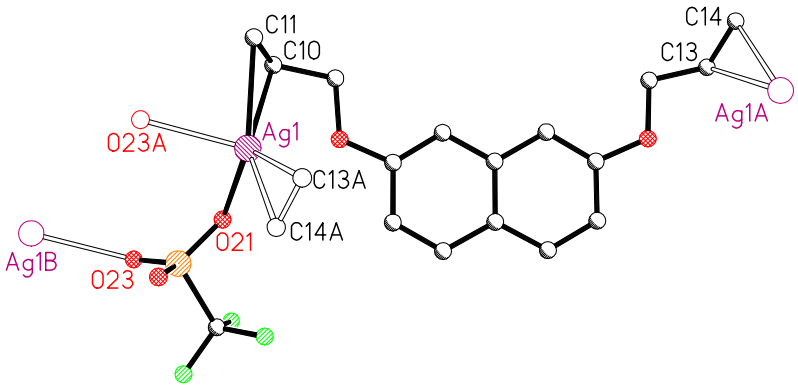
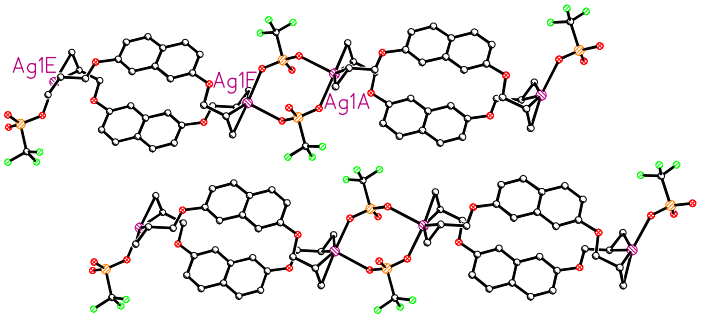
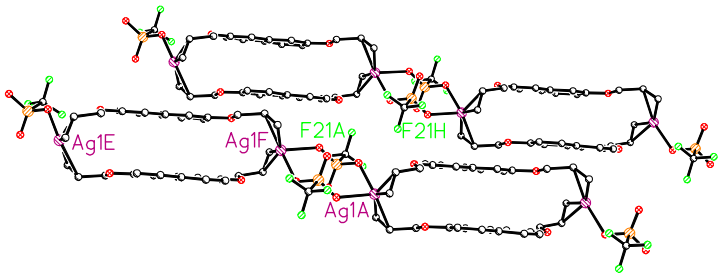


Figure 3.31 *- View of the asymmetric unit of* ***3.22****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C10 2.514(3), Ag1-C11 2.543(3), Ag1-C10,C11 2.440(3), Ag1-C13A 2.477(3), Ag1-C14A 2.390(3), Ag1-C13A,C14A 2.342(3), Ag-O21 2.381(2), Ag1-O23 2.463(2), C10,C11-Ag1-C13A,C14A 133.8(1), C10,C11-Ag1-O21 115.5(1), C10,C11-Ag1-O23A 86.81(9), C13A,C14A-Ag1-O21 105.2(1), C13A,C14A-Ag1-O23A 116.6(1), O21-Ag1-O23A 88.91(7).*

Similar to the previous structure, **3.17** with two bridging triflate anions, the silver in this complex also has distorted trigonal pyramidal geometry with a calculated τ_4 value of 0.78. Two oxygen atoms from different triflate counter anions are coordinated and, in this case, two alkenes from the allyl ether arms are coordinated rather than one alkene and one η^2 arene as in **3.17**. The Ag···Ag separation across ligand**3.13**, Ag1E and Ag1F in Figure 3.32(a,b) is 12.31 Å and is, as expected, much greater than the 8.45 Å Ag···Ag separation seen across the related *meta* ligand **2.8** in complex **2.15**. The Ag···Ag separation between silver atoms doubly bridged by triflate anions, Ag1A and Ag1F, is 5.88 Å which is marginally longer than the Ag···Agdistance of 5.22 Å between two silver atoms bridged by a single triflate counter anion in **3.17**.



a)



b)

Figure 3.32 *– View of two neighbouring strands of the one-dimensional polymer* ***3.22****. Hydrogen atoms have been omitted for clarity.* ***a)*** *Looking at the silver atoms doubly bridged by the triflate anions* ***b)*** *same polymer strands rotated 90 º viewing the silver atoms doubly bridged by ligand* ***3.13****.*

The silver atoms are alternately doubly bridged by molecules of **3.13** and then doubly bridged by two triflate anions to form a one-dimensional polymer. Figure 3.32 displays the one-dimensional polymeric character of **3.22**. Another way to describe this polymer is to say that it is a chain of [2+2] macrocycles, consisting of two silvers that are doubly bridged by two molecules of **3.13**, which in turn are linked together by bridging counter anions.

The naphthalene rings within each macrocycle π-π stack in a staggered arrangement with respect to each other (3.60-3.62 Å) and also interact with macrocycles from neighbouring polymer strands in a similar manner (3.39 Å). Triflate fluorine atoms, as in **3.17**, are forced into close proximity. The shortest distance between fluorine atoms on adjacent triflate anions is 2.827(8) Å and again arises from close crystal packing rather than attractive F···F interactions.[135-138]

3.9 Complexes of 2,2'-Di(allyloxy)-1,1'-binaphthalene

With silver perchlorate (**3.23**) and (**3.24**)

The racemic mixture **3.14a** was initially used and was successfully reacted with silver(I) perchlorate in a chloroform/acetone solution. The resulting crystalline product, **3.23**, was analysed by X-ray crystallography and solved in the monoclinic space group $P2_1/c$. This space group is centrosymmetric which confirms the presence of both complex enantiomers within the same crystal. The asymmetric unit contains one ligand, two silver atoms, two coordinated counter anions, two coordinated acetone molecules and one solvent molecule with an overall discrete M_2L structure.

While the R(int) and R(sigma) values are acceptable the R_1 value is high. This is likely due to other solvent molecules that were lost previous to, or during, the data collection leaving unassignable electron density in the difference map. A second data collection was done on a different crystal with similar problems occurring.

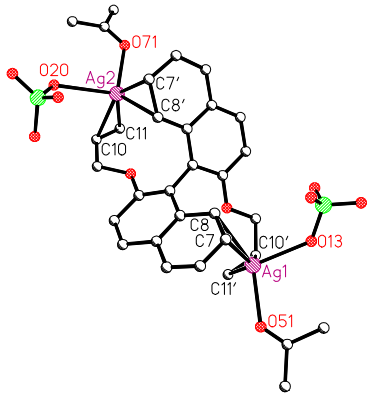
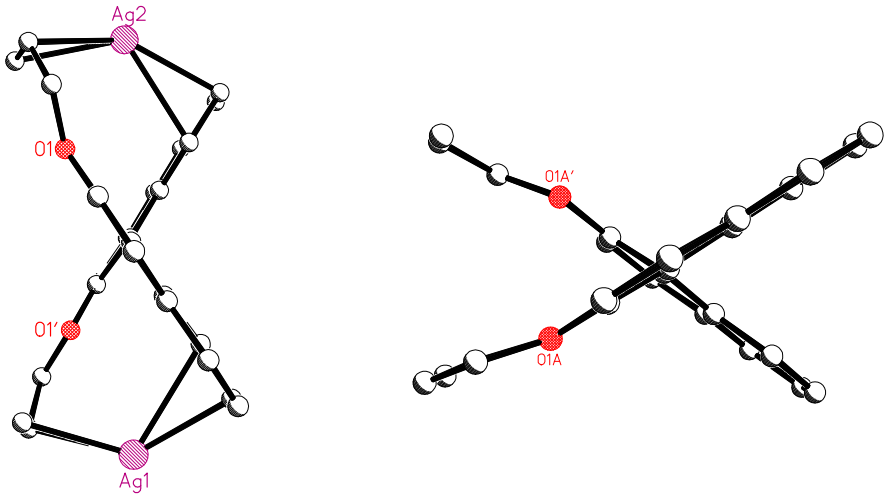


Figure 3.33 *– View of the core unit of complex* ***3.23****. Bond lengths and angles are not displayed due to poor refinement.*

Both silver units are four coordinate with approximate trigonal pyramidal geometry. Each silver atom has one ligand **3.14a** coordinated to it through an alkene on the allyl ether arm and through η^2 coordination of the naphthalene ring at the C7,C8 position. The perchlorate counter anion is coordinated to the silver atom through one of its oxygen atoms and the perchlorate anion coordinated to Ag2 is disordered over two positions. Each silver atom also has an acetone coordinated through the carbonyl oxygen acting as an auxiliary ligand. The Ag···Ag separation acrossligand **3.14a** is approximately 9 Å.

Ligand **3.14a** chelates to two silver atoms through an alkene of the allyl ether arm and through the naphthalene ring at the C7,C8 position. This chelation has a significant effect on the dihedral angle between the two naphthalene rings as seen in Figure 3.34.

The acute torsion angle in the free ligand **3.14b** is between the two ends of the naphthalene ring containing the allyl ether substituents whereas in the complex the acute angle is between a substituted and unsubstituted end. The torsion angle between the naphthyl rings changes from 68.9 º in the free ligand to approximately 110 º in the coordinated ligand. This change in angles occurs to accommodate the chelation of ligand **3.14a** to silver.



a) ***b)***

Figure 3.34 *– Comparison of the torsion angle between the naphthalene rings in ligand* ***3.14****.* ***a)*** *View of the coordinated ligand looking down the transannular bond* ***b)*** *view of the free ligand* ***3.14b*** *also looking down the transannular bond.*

Again, the η^2 coordination occurs on a predicted position on the naphthalene ring and in this case the C7,C8 position. As in the previous examples of coordination at a localised double bond, it leads to elongation, however due to the poor refinement there are large error values on bond lengths within the structure and a definitive comparison cannot be made.

Within the crystal packing there is alternating staggered, then edge-to-face π-π stacking interactions. There is also weak hydrogen bonding interactions between the hydrogen atoms on **3.14a** and the perchlorate oxygen atoms. The chloroform molecule is held in place by weak hydrogen bonding between its hydrogen and an oxygen atom from a perchlorate as well as between the chlorine atoms and a hydrogen on a coordinated acetone.

The enantiomerically pure **3.14b** and silver(I) perchlorate was also successfully reacted together under the same conditions as the racemic ligands. Again the crystalline product,

3.24, was analyzed by X-ray diffraction and this time the structure solved in the monoclinic chiral space group C2. The basic ligand/silver motif of this complex is the same as in **3.23**. The structure is a discrete M_2L complex with each ligand chelating to two silver atoms via an alkene on an allyl ether arm and an η^2 coordination at the C7,C8 position on the naphthalene ring.

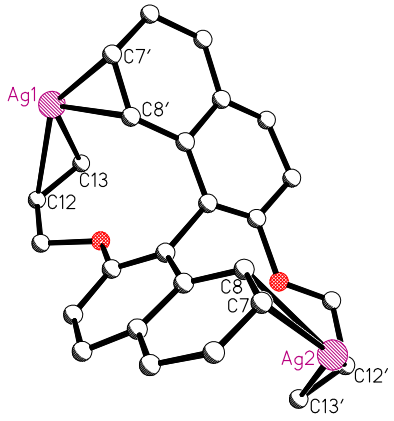


Figure 3.35 *– View of the core structure of complex* ***3.24****.*

The differences between **3.23** and **3.24** lie in the position of the counter anions and solvent molecules. The asymmetric unit of **3.24** contains one ligand, two silver atoms and one coordinated perchlorate and two half perchlorate anions, one of which is also coordinated. It is not certain whether the full perchlorate also coordinates to the second silver. There are no definable solvent molecules and there are no coordinated acetone molecules acting as auxiliary ligands. However it is difficult to say this definitively, as there is still unassigned electron density in the electron difference map which is likely to be disordered solvent molecules. The dihedral angle, as in **3.23**, is much greater in **3.24** than the free ligand.

The three-dimensional packing is difficult to define because of the unassigned electron density in the electron difference map which is likely to be disordered solvent molecules.

3.10 Summary

This chapter details the synthesis of seven previously unknown compounds, six of which are disubstituted allyl ethers around a naphthalene core and one chiral ligand based on a 1,1'-binaphthyl-2,2'-diol core. The coordination chemistry of these ligands with a variety of silver(I) salts, with coordinating or non-coordinated counter anions was explored. A total of nine complexes were isolated and studied by single crystal X-ray diffraction.

A variety of topologies is achieved with this ligand series ranging from discrete structures to two-dimensional polymers. Complexes **3.18** and **3.19** are discrete [2+2] macrocycles formed from ligand **3.10** with silver(I) triflate or silver(I) perchlorate, respectively. Ligands **3.14a** and **3.14b** give similar discrete M_2L structures when combined with silver(I) perchlorate. Four one-dimensional polymers were formed. Ligand **3.8** gave a simple folded one-dimensional polymer with silver(I) perchlorate, **3.17** is a complicated one-dimensional polymer with ligand **3.9** bridging four silver atoms. Ligand **3.11** when combined with silver(I) hexafluorophosphate alternatively doubly bridges silver atoms via η^2 and oxygen interactions then doubly bridges by two allyl ether arms to give a one-dimensional polymer. Ligand **3.13** gave a one-dimensional polymer with silver triflate where the silver atoms are alternately doubly bridged by two ligands **3.13** then doubly bridged by two triflate counter anions. Ligand **3.12** forms a two-dimensional polymer when combined with silver tetrafluoroborate.

Silver atoms generally have either distorted trigonal planar or distorted tetrahedral geometry with at least two, but no more than three, double bonded carbon moieties coordinated. There are three instances of silver disorder occurring in complexes **3.16**; **3.19** and **3.20**. This is a reflection of the many competing interactions such as silver-oxygen, silver-alkene and silver-arene bonding within these compounds. Silver-silver separation is effectively controlled by the use of varying disubstitution patterns around the naphthalene core. A range of silver-silver distances is achieved with a shortest distances of 7.0 Å in **3.19** to the longest of 13.8 Å in **3.21**, measured across the longest axis of the ligand.

Silver-alkene bonds are more favoured than silver-arene and silver-ethereal oxygen bonds as it is present in all of the structures reported in this chapter. It is the only interaction found between silver and the organic ligand **3.13** in **3.22**. Silver-arene bonds are favoured to a lesser degree than silver-alkene but more so over than silver-ethereal oxygen bonds. Seven out of nine structures have silver-arene bonds but always in conjunction with silver-alkene bonds. Silver-ethereal oxygen bonds are the least favoured out of the three and are only seen in two structures **3.16** and **3.20**. In **3.16** the silver was disordered and one of the positions allowed it to interact with the ethereal oxygen. This position had only 5 % occupancy and the silver did not have to sacrifice any bonding to a nearby alkene. The second example **3.20** also had disorder in the silver atom where the two positions either bonded to one ethereal oxygen, or chelated to two of them.

The η^2 coordination of naphthalene to silver occurred on the shorter carbon-carbon bonds; C1-C2, C3-C4, C5-C6 or C7-C8 in complexes **3.17**, **3.18**, **3.19**, **3.21**, **3.23** and **3.24**. In complexes **3.17** and **3.21** a single naphthalene ring is coordinated to two different silver atoms via η^2 interactions. In the above examples the bond lengths between carbons involved in the η^2 coordination are slightly longer compared to the free ligand. A notable exception occurs in **3.20**, where naphthalene coordinates to a silver atom through a longer carbon-carbon bond C3-C4. Interestingly the C3-C4 bond length in **3.20** is unusually short compared to the free ligand suggesting increased localization of the double bond at this position.

Chapter Four

Multiply Armed Ligands with Benzene Cores

CHAPTER 4

Multiply Armed Ligands with Benzene Cores

4.1 Introduction

As demonstrated in previous chapters, silver centres are limited to coordinating only two or three olefins at one time. This allows it to act only as a two or three connecting node. To include higher degrees of connectivity into these systems the ligand itself can be modified by adding additional functional groups. With higher denticities the ligand is able to act as a three, four or six connecting node. In this way new structures with different topologies can be formed.

This methodology is demonstrated by the family of polypyridyl ligands; **4.1**,[93] **4.2**,[139,140] **4.3**,[97,141] **4.4**,[141] **4.5**[142] and **4.6**,[143,144] shown in Figure 4.1, which are based around a benzene core and use pyridine moieties as the metal donor.

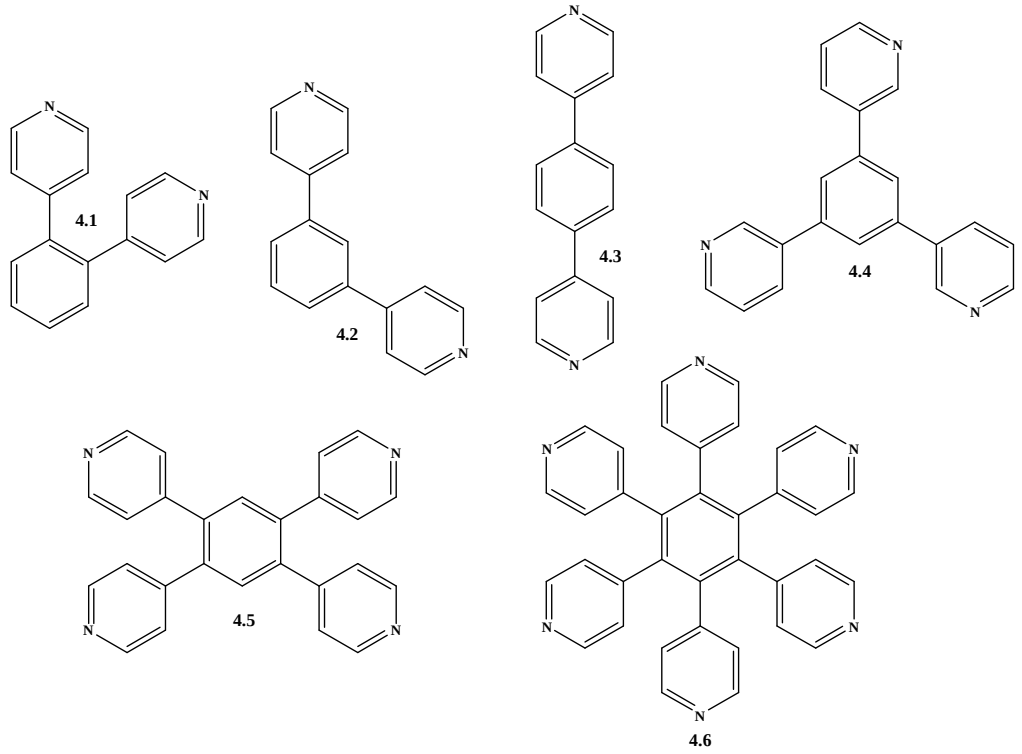


Figure 4.1 *– Family of pyridyl ligands with varying denticities.*

Ligands **4.1**, **4.2** and **4.3** act as two connecting nodes and increasing this from two to three, or more, connector nodes can influence the resulting structure. For example, when **4.2** is combined with CuI, which acts as a three connecting node, the resulting structure is a one-dimensional ribbon[140] as in Figure 4.2(a). When **4.4** is combined with a three connecting node, in this instance $Cu(NO_3)_2$ in conjunction with monoethanolamine, a ladder type structure is formed[141] as in Figure 4.2(b). Another example is when ligand **4.2** is combined with four coordinate Pd(II) ions it forms a discrete roughly spherical $M_{12}L_{24}$ structure.[145] Ligand **4.5**, when combined with four coordinate Cu(II) ions, forms polymeric assemblies including two- and three-dimensional networks some of which are interpenetrated.[145] Although the synthesis of ligand **4.6** has been reported[143,144] there are yet to be any papers published to describe its chemistry with transition metals.

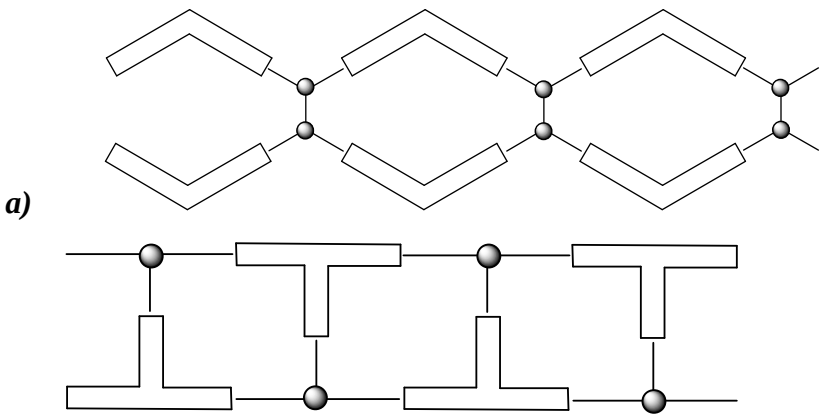


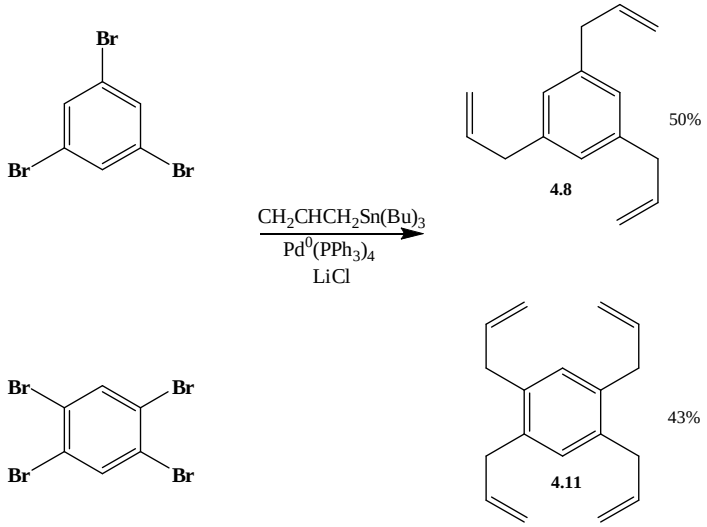
***Figure 4.2** – **a)** Schematic of ribbon structure comprised of a bent bridging ligand and a three connecting metal ion **b)** schematic of a ladder type structure comprised of two different three connecting nodes.*

This chapter discusses the results of the silver(I) chemistry of a series of three tridentate ligands, four tetradentate ligands and one hexadentate ligand. As an extension of the work in chapter two, spacer atoms have also be incorporated into the ligand series. Ligands are; 1,3,5-trivinylbenzene (**4.7**), 1,3,5-triallylbenzene (**4.8**), 1,3,5-tri(allyloxy)benzene (**4.9**), 1,2,4,5-tetravinylbenzene (**4.10**), 1,2,4,5-tetraallylbenzene (**4.11**), 1,4-di(allyloxy)-2,5-

diallylbenzene (**4.12**), 1,2,4,5-tetraallylbenzoquinone (**4.13**) and 1,2,4,5-tetraallyl 3,6-di(allyloxy)benzene (**4.14**).

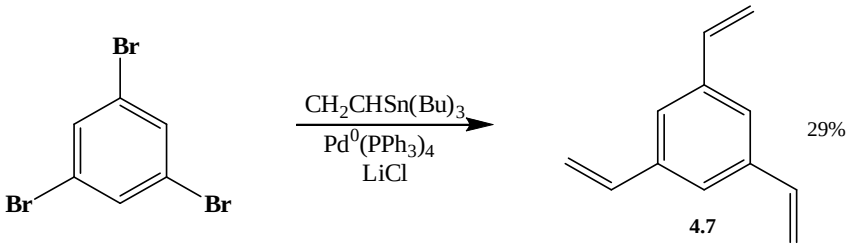
4.2 Ligand Syntheses

The syntheses of **4.8** and **4.11** were carried out using the same methodology as was used for the synthesis of the diallylbenzene isomers. The appropriate bromobenzene precursor was heated to 100 °C and reacted with three and a third equivalents of allyltributylstannane for **4.8** or four and a half equivalents for **4.11**. Again tetrakis-(triphenylphosphine)palladium(0) was used as the catalyst and similar reaction times to the diallylbenzenes were needed.



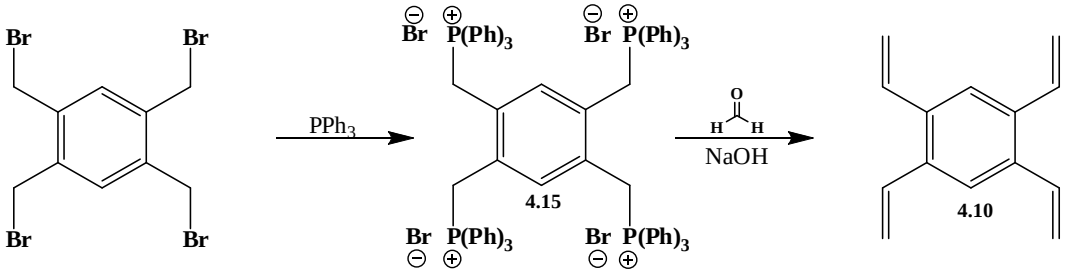
***Scheme 4.1** – Stille coupling reactions to give ligands **4.8** and **4.11**.*

Similar to the diallylbenzene ligands, **4.7** was synthesised via a three-fold Stille coupling between 1,3,5-tribromobenzene and vinyltributylstannane. Ligand **4.7** is a known compound and the synthesis was taken directly from a literature procedure.[108] The synthesis is the same as for ligands, **4.8** and **4.11**, except the coupling reagent used is vinyltributylstannane and the reaction time is shorter at 18 hours.



Scheme 4.2 *– Stille coupling reaction to give ligand* ***4.7****.*

A slightly different approach was taken in the synthesis of **4.10**, by utilising the Wittig reaction. In this case, the phosphonium reagent was based on the ligand core itself and the carbonyl component was formaldehyde. The phosphonium precursor is prepared by refluxing triphenylphosphine with 1,2,4,5-tetra(bromomethyl)benzene in acetone to give intermediate **4.15** in Scheme 4.3. This is then reacted with formaldehyde in the presence of base to give **4.10** in low yield.



Scheme 4.3 *– Reaction scheme for the synthesis of ligand* ***4.10****.*

More care was necessary in the synthesis of **4.9** than the previous allylations of the dihydroxy-benzenes and -naphthalenes as there is a greater probability of allylation occurring at a carbon on the six membered ring and not on the oxygen as shown in Figure 4.3.

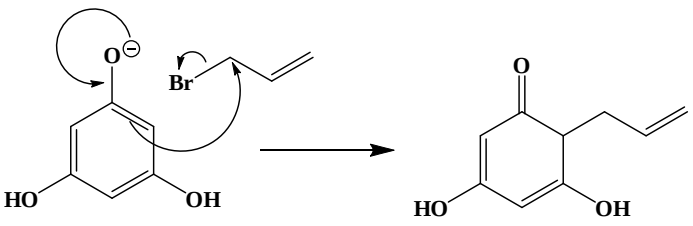
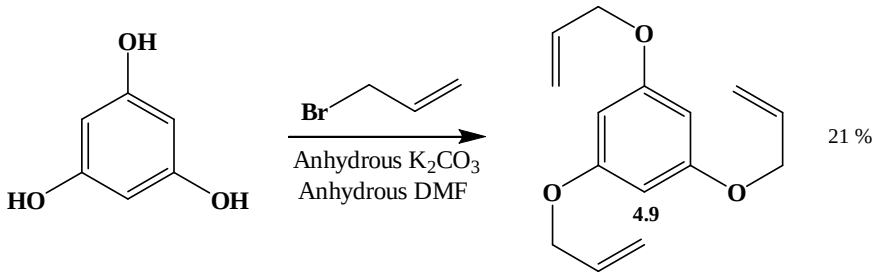


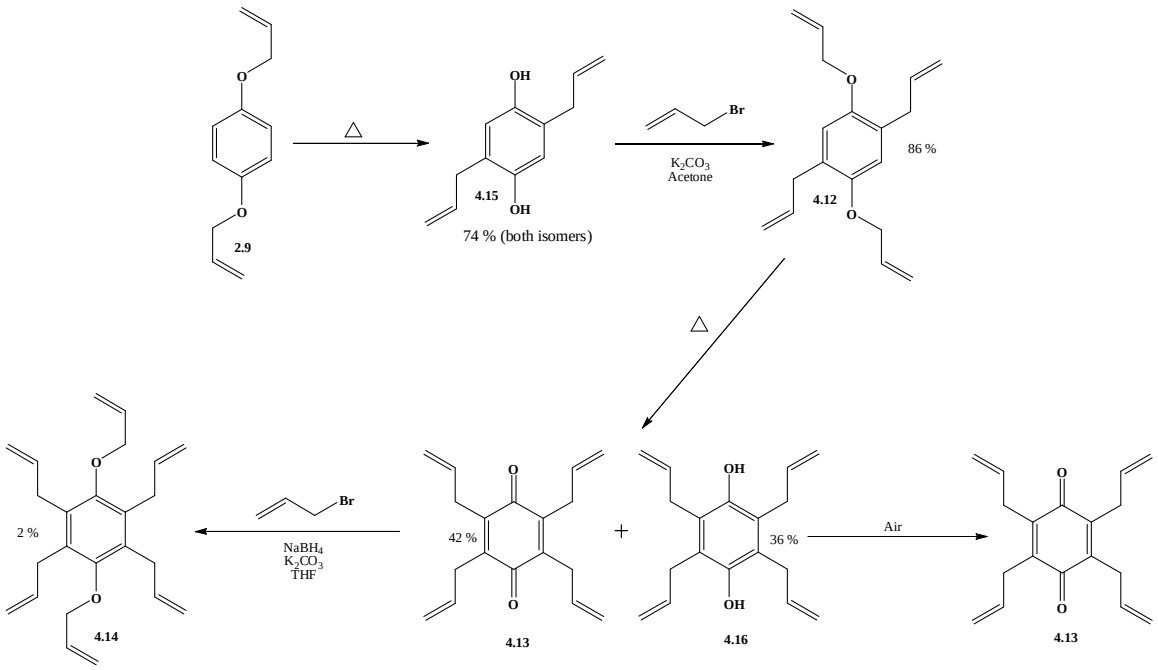
Figure 4.3 *– Possible carbon allylation.*

As an alternative method **4.9** was synthesised following a literature procedure. This involved heating phloroglucinol and anhydrous potassium carbonate in anhydrous dimethylformamide at 65 °C for an hour prior to the addition of four equivalents of allyl bromide. The mixture was then heated for a further 38 hours.



Scheme 4.4 *– Oxygen allylation reaction.*

A complicated multi-step synthesis was employed to create ligand **4.14** during which two other ligands, **4.12** and **4.13**, are formed as intermediates. Initially, ligand **2.9** was heated to initiate a double Claisen rearrangement giving two isomers, of which only one, **4.15**, is shown in Scheme 4.5. Both isomers then underwent a double allylation under the same reaction conditions that yields ligand **2.9** to give ligand **4.12**. Ligand **4.12** then undergoes a second double Claisen rearrangement which is carried out neat and under argon, yielding a 50% mixture of **4.13**, and **4.16**. Compound **4.16** is very air sensitive and converts rapidly to **4.13** upon standing. In situ reduction of **4.13** by sodium borohydride to **4.16** allows further allylation of the hydroxyl groups to give ligand **4.14**. The yield of **4.14** is very low at only 2 % for the last reaction, with only enough sample isolated for characterisation.



Scheme 4.5 *– Reaction scheme for the synthesis of ligands* ***4.12***, ***4.13*** *and* ***4.14****.*

THREE ARMED LIGANDS

There was limited success with the three armed ligand series with only **4.7** forming complexes with silver(I). Ligand **4.7** has the more rigid functional arms of the tridentate ligands and the other two, **4.8** and **4.9**, may have too much flexibility to form crystalline complexes. Another possibility is that three armed ligands are incompatible with silver(I) but further evidence for this conclusion is needed.

4.3 Complexes of Trivinylbenzene

With silver(I) perchlorate (**4.17**)

The crystalline product (**4.17**) from the reaction of ligand **4.7** and silver(I) perchlorate mixed in a 1:1 ratio solved in the monoclinic space group P2/c. The asymmetric unit, shown in Figure 4.4, revealed the product has a 3:2 silver to ligand ratio containing one and a half silver atoms and one molecule of **4.7**. Additionally, there is one perchlorate anion as well as a second half perchlorate anion which shares 50 % occupancy with a

water molecule. The O4 from the perchlorate and the O4’ of the water molecule share the same position. One of the silver atoms, Ag2, lies on a special position.

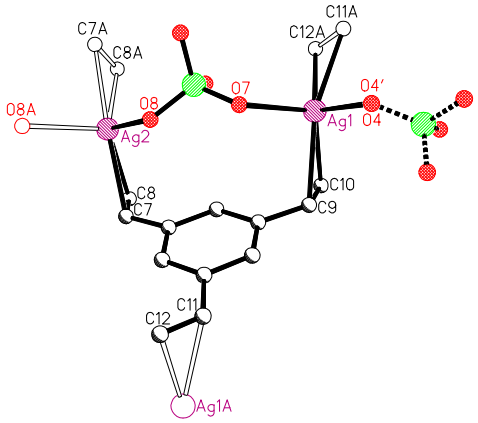


Figure 4.4 *– Asymmetric unit of complex* ***4.17****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C9 2.502(6), Ag1-C10 2.388(7), Ag-C9,C10 2.354(7), Ag1-C11A 2.476(8), Ag1-C12A 2.375(8), Ag1-C11A,C12A 2.349(8), Ag1-O4 2.424(6) Ag1-O4’, Ag1-O7 2.535(6), Ag2-C7 2.435(6), Ag2-C8 2.354(6), Ag2-C7,C8 3.299(6), Ag2-C7A 2.435(6), Ag2-C8A 2.354(6), Ag2-C7A,C8A 3.299(6), Ag2-O8 2.521(5), Ag2-O8A 2.521(5), O4-Ag1-O7 84.1(2), O4-Ag1-C9,C10 106.13(3), O4-Ag1-C11A,C12A 105.5(3), O7-Ag1-C9,C10 103.6(2), O7-Ag1-C11A,C12A 114.8(3), C9,C10-Ag1-C11A,C12A 132.0(3), O8-Ag2-O8A 87.1(2) O8-Ag1-C7,C8 100.8(2), O8-Ag1-C7A,C8A 110.1(2), O8A-Ag1-C7,C8 110.1(2), O8A-Ag1-C7A,C8A 100.8(2), C7,C8-Ag1-C7A,C8A 137.0(4).*

There are two crystallographically independent silver atoms Ag1 and Ag2 in **4.17**, both of which are four coordinate with two olefins and two oxygen atoms coordinated. The two oxygen atoms coordinated to Ag2 are from two separate perchlorate counter anions. Ag1 however, has one oxygen atom from a perchlorate anion and the other is a shared position comprised of an oxygen atom from a water molecule or an oxygen atom from a second perchlorate anion each having 50 % occupancy. The geometries of the two silver atoms

are similar with the largest angle between the two coordinated olefinic moieties and the smallest between the two coordinated oxygen atoms. The calculated τ_4 value of both Ag1 and Ag2 is 0.80 indicating a distorted trigonal pyramidal geometry.

The vinyl groups in vinylbenzenes have a tendency to lie in, or close to, the plane of the benzene ring to extend the conjugation of the aromatic ring to the olefin. This preference for the vinyl group to lie within the plane restricts the free rotation and ultimately the conformations it adopts in the solid state. It can either have the terminal olefinic carbon pointing to the ‘left’ or to the ‘right’ as in Figure 4.5.

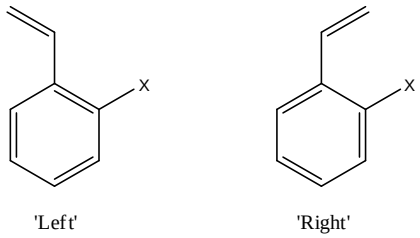


Figure 4.5 *– Two likely solid state conformations of a vinylbenzene, x = a point of reference.*

The possible solid state conformations are increased when silver(I) is coordinated, as it can reside either above or below the plane of the molecule. In this way the Ag···Ag separation is influenced not only by the substitution pattern around the benzene ring but also the solid state conformation of the vinyl group and whether the coordinated silver atoms are on the same side or opposing sides of the vinylbenzene.

Ligand **4.7** acts in a tridentate manner in **4.17** with all three olefins coordinated to three different silver atoms. It can be viewed as three sets of vinyl arms in a *meta* relationship. Each of the three sets of *meta* vinyl arms within this complex have a different conformation. The olefinic carbons; C7,C8 and C9,C10 (Figure 4.4) both point toward each other, C9,C10 and C11,C12 both point away from each other and C7,C8 and C11,C12 have one pointing towards and one pointing away from each other. The complexity increases when the coordinated silver atoms are taken into account as they can coordinate either above or below the plane of the ligand with respect to each other. In

this instance C7,C8 and C9,C10 have both silver atoms residing on the same side of **4.7** with the shortest Ag···Ag separation between Ag1 and Ag2 in Figure 4.4 with a distance of 5.70 Å. This type of coordination is analogous to the way in which *meta*-divinylbenzene interacts with silver(I) perchlorate,[95] as shown in Figure 4.6, and has a very similar Ag···Ag separation of 5.66 Å. Olefinic carbon atoms C7,C8 and C11,C12 have coordinated silver atoms residing on opposite sides of **4.7**, Ag1A and Ag2 in Figure 4.4, and have a Ag···Ag separation of 8.01 Å. Carbons C9,C10 and C11,C12 have the longest Ag···Ag separation, Ag1A and Ag2 in Figure4.4, as both olefins point away from each other and the coordinated silver atoms reside on opposite sides of **4.7** giving a distance of 8.47 Å.

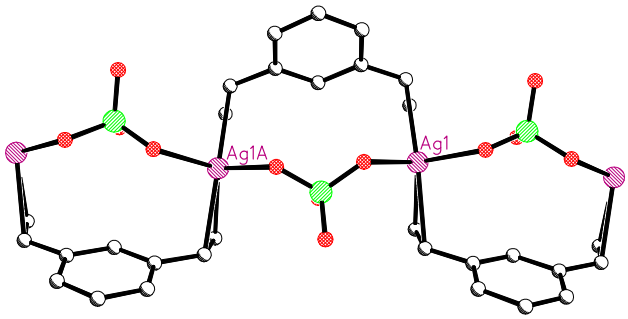


Figure 4.6 *– One-dimensional coordination polymer of* ***1.27*** *and silver(I) perchlorate. Hydrogen atoms have been omitted for clarity.*

Complex **4.17** is a one-dimensional metallopolymer with some structural similarities to the coordination polymer formed between **1.27** and silver perchlorate, Figure 4.6. Complex **4.17** has same bridging motif with a perchlorate and two *meta* vinyl arms doubly bridging two silver atoms. However unlike in **1.27** it does not form a continuous chain as it is capped by either a water molecule or perchlorate anion after one repetition, see Figure 4.7(a). The polymer can be described as an offset ladder type structure, see Figure 4.7(b), if only the interactions between ligand **4.7** and silver are taken into account. In this complex, ligand **4.7** is acting as a three connecting node in combination with silver acting as a linear two connecting unit. The metallopolymer is not flat as it appears in Figure 4.7(a) but undulates when viewed from the side as seen in Figure 4.7(c).

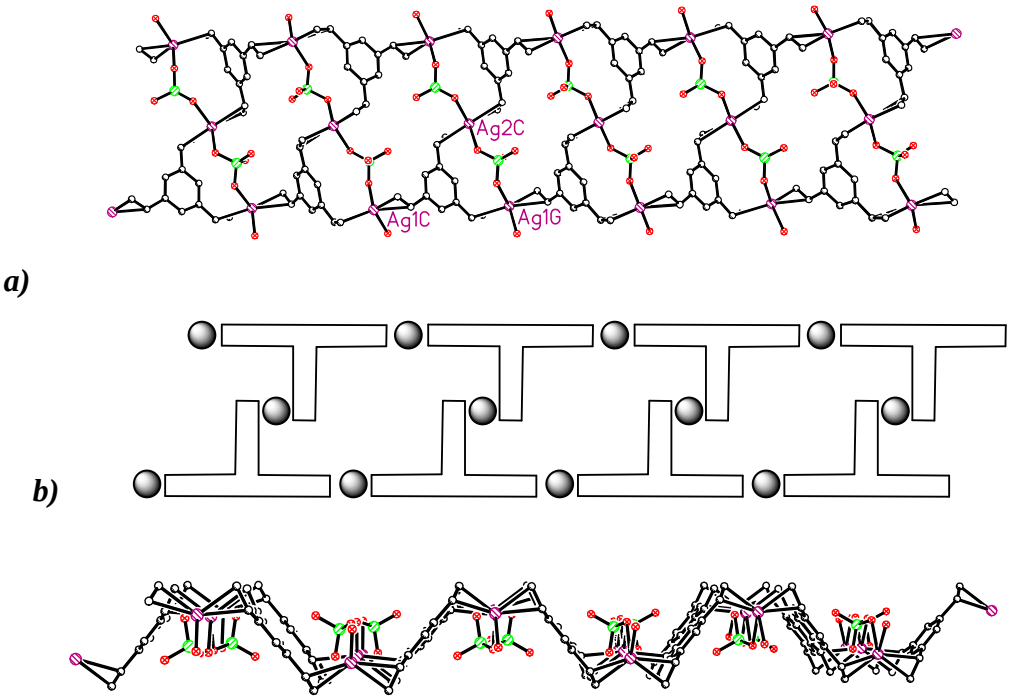


Figure 4.7 *– Section of the one-dimensional polymer* ***4.17****. Only the coordinated oxygen atom of the terminal perchlorate is shown and hydrogen atoms have been omitted.* ***a)*** *Birds eye view of metallopolymer* ***b)*** *schematic representation of offset square ladder type one-dimensional polymer* ***c)*** *side view showing undulation of the metallopolymer.*

The polymer strands stack directly above and below each other with weak hydrogen bonding interactions between oxygen atoms on the perchlorate anion and hydrogen atoms on ligand **4.7** (2.40 – 2.68 Å).

FOUR ARMED LIGANDS

4.4 Complexes of Tetravinylbenzene

With silver(I) perchlorate (**4.18**)

Ligand **4.10** can be broken down into one of three ways; one, to see it as having two sets of vinyl arms in a *para* relationship, secondly as having two set of vinyl arms in a *meta* relationship or finally having two sets of vinyl arms in an *ortho* relationship. It is more

conformationally restricted than **4.7** as the vinyl groups in the ortho relationship cannot point towards each other due to steric hindrance. Three complexes of ligand **4.10** have been isolated in which two show **4.10** to interact with silver in an analogous manner to *meta*- and *para*-divinylbenzene. In all three complexes ligand **4.10** has a very similar conformation of the vinyl groups.

When reacted with silver(I) perchlorate ligand **4.10** forms a crystalline complex within hours. Upon X-ray analysis it solved in the orthorhombic space group Pmna. The asymmetric unit, shown in Figure 4.8, is sparsely populated containing only a quarter of a molecule of **4.10**, half a silver atom and half a coordinated perchlorate anion. The silver atom, Ag1, chlorine atom, Cl1, two oxygen atoms, O1 and O2, and carbon atom, C2, all lie on special positions. Ligand **4.10** lies on a mirror plane and a two-fold rotation axis.

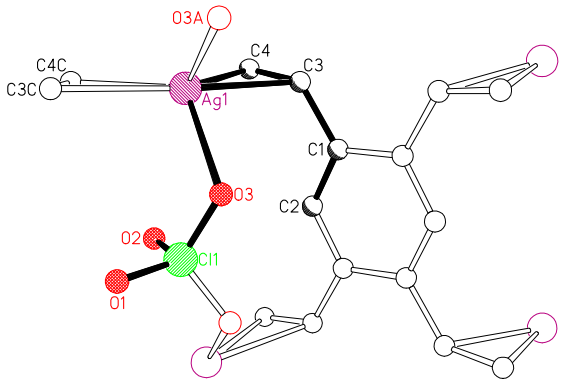


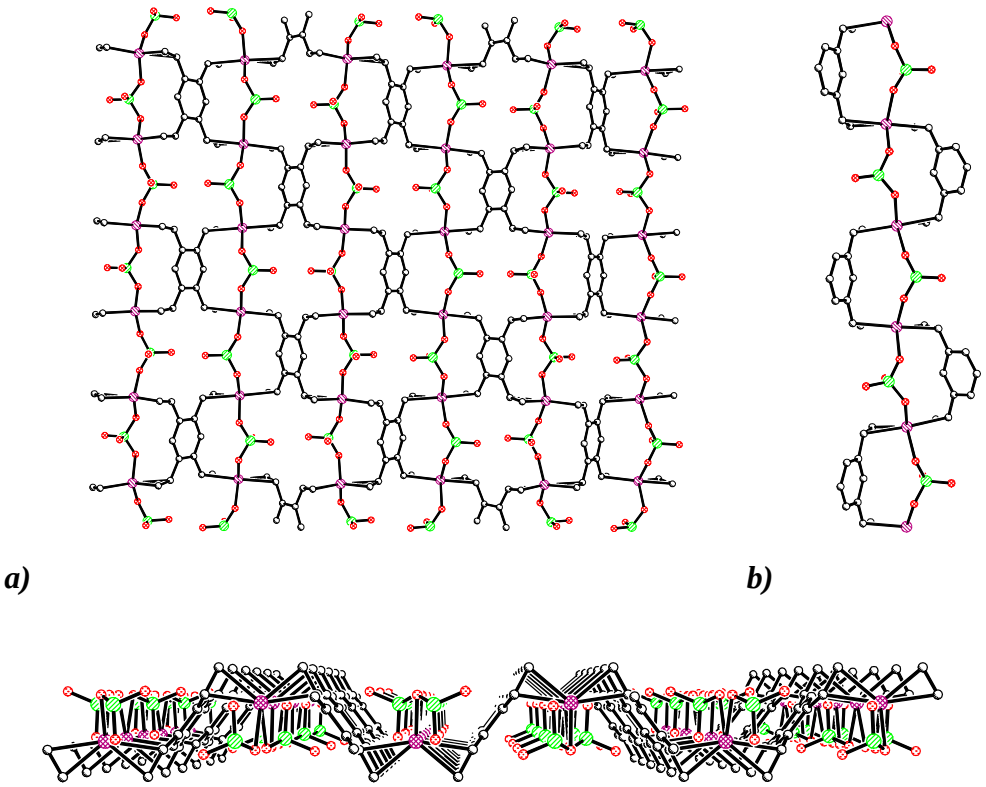
Figure 4.8 *– Asymmetric unit of complex* ***4.18****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C3 2.454(5), Ag1-C4 2.362(5), Ag1-C3,C4 2.313(5), Ag1-C3C 2.454(5), Ag1-C4C 2.362(5), Ag1-C3C,C4C 2.313(5), Ag1-O3 2.514(4), Ag1-O3a 2.514(4), O3-Ag1-O3A 75.3(2), O3-Ag1-C3,C4 108.36(2), O3A-Ag1-C3,C4 109.38(2), O3-Ag1-C3C,C4C 109.38(2), O3A-Ag1-C3C,C4C 108.36(2), C3,C4-Ag1- C3C,C4C 131.8(3).*

The silver atoms are four coordinate with two oxygen atoms from two different counter anions and two vinyl groups coordinated. The calculate τ_4 value for Ag1 is 0.84 which indicates a trigonal pyramidal geometry but visual inspection reveals that it is more appropriate to consider the geometry as distorted tetrahedral. The two angles that are distorted from tetrahedral are between the two coordinated oxygen atoms, 75.3 °, and between the two coordinated vinyl groups, 131.8 °.

In complex **4.18** the two sets of *para* and *ortho* vinyl groups have silver atoms on opposing sides and the *meta* groups have the silver atoms on the same side of the ligand. The Ag···Ag separations are as follows: *para* 8.72 Å, *ortho* 6.81 Å, *meta* 5.45 Å. The *meta* distance is slightly shorter than in **4.17** which can be accounted for by variations in which the vinyl groups slightly twist out of the plane. The *meta* separation is also shorter than the *ortho* which is accounted for by the conformations of coordinated silver atoms.

The overall structure of **4.18** is a highly symmetrical two-dimensional metallopolymer, which is shown in Figure 4.9(a). Ligand **4.10** interacts with silver(I) perchlorate in a manner analogous to *meta*-divinylbenzene which forms the one-dimensional polymer with silver(I) perchlorate shown in Figure 4.9(b). With the greater denticity of **4.10** the same structural motif is repeated on both sides of the ligand giving a two-dimensional polymer opposed to a one-dimensional one. As in **4.17** the two-dimensional sheet is not flat and when viewed from the side the zig-zag shape becomes apparent.

The two-dimensional sheets stack directly above and below each other with weak hydrogen bonding between the oxygen atoms on the perchlorate anion and hydrogen atoms on **4.10** (2.64 - 2.69 Å).



a) ***b)*** ***c)***

Figure 4.9 – a) *Two-dimensional metallopolymer* ***4.18*** ***b)*** *one-dimensional polymer formed from meta-divinylbenzene and silver(I) perchlorate* ***c)*** *side view of the two-dimensional sheet showing the zig-zag nature. Hydrogen atoms have been omitted for clarity.*

The reaction of ligand **4.10** and silver(I) perchlorate carried out under very similar conditions gives a second compound (**4.19**). This compound was isolated after the solvent was allowed to evaporate over a period of days while **4.18** crystallises out of solution within hours, indicating **4.19** is the thermodynamic product. The second compound **4.19** solves in the triclinic space group P-1 with a 1:4 ligand to silver ratio. There are less symmetry elements in **4.19** with half a molecule of **4.10** and two silver atoms, as well as their associated counter anions, in the asymmetric unit as shown in Figure 4.10.

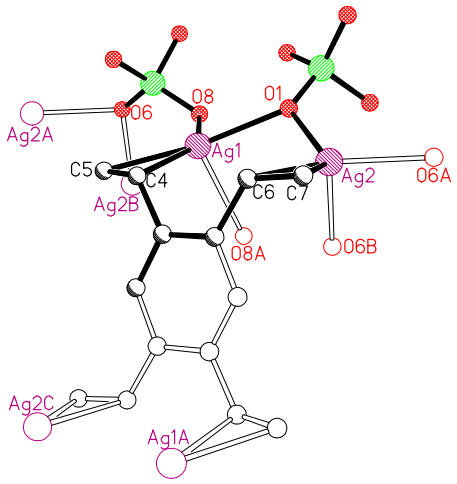
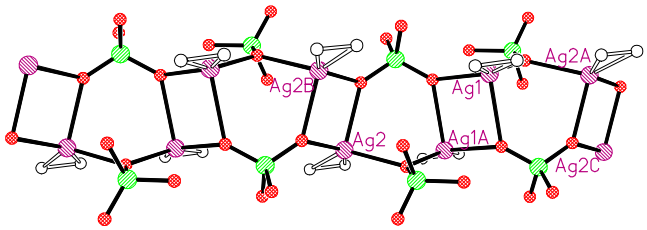


Figure 4.10 *– Contents of the asymmetric unit of* ***4.19****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C4 2.365(4), Ag1-C5 2.336(4), Ag1-C4,C5 2.252(4), Ag1-O1 2.293(3), Ag1-O8 2.386(3), Ag1-O8A 2.559(3), Ag2-C6 2.354(4), Ag2-C7 2.306(4), Ag2-C6,C7 2.230(4), Ag2-O1 2.332(3), Ag2-O6A 2.308(3), Ag2-O6B 2.408(3), O1-Ag1-O8 90.1(1), O1-Ag1-O8A 88.5(1), O1-Ag1-C4,C5 136.6(2), O8-Ag1-O8A 87.3(1), O8-Ag1-C4,C5 90.1(1), O8A-Ag1-C4,C5 107.0(1), O1-Ag2-O6 107.4(1), O1-Ag2-O6B 89.5(1), O1-Ag2-C6,C7 121.0(2), O6A-Ag2-O6B 86.8(1), O6A-Ag2-C6,C7 126.05(1), O6B-Ag2-C6,C7 114.26(1).*

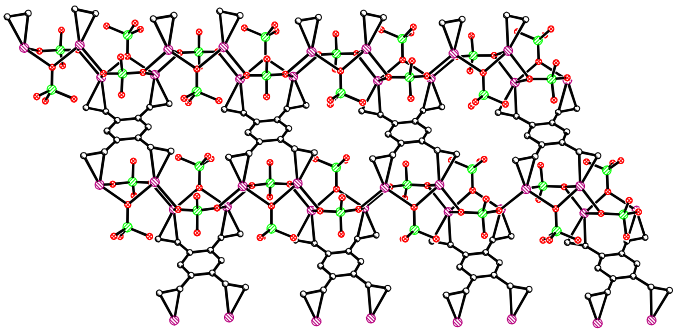
Both crystallographically independent silver atoms, Ag1 and Ag2, are four coordinate and, unlike **4.18**, each silver has only one olefinic group coordinated. The rest of the coordination sphere is comprised of oxygen atoms from perchlorate counter anions. Ag1 has a geometry closer to trigonal pyramidal while Ag2 has a geometry closer to tetrahedral. As in **2.12**, where there is only one coordinated olefin to a silver atom, the distance between the C=C centroid and silver is shorter at 2.25 Å and 2.23 Å for Ag1 and Ag2 respectively.

Ligand **4.10** lies on a centre of inversion with a half molecule in the asymmetric unit. The solid state conformation of the vinyl arms in **4.19** is similar to **4.18** and it too acts as a tetradentate ligand. However the conformation of the coordinated silver atoms differs in **4.19** in that the silver atoms lie on the same side of the *ortho* pair of vinyl arms as opposed to the *meta* pair in **4.18**. Both sets of *para* vinyl arms have the silver atoms on opposite sides of **4.10** similar to **4.18**. As expected the Ag···Ag separation across the*meta* arms is longer than in **4.18** at 7.69 Å and the Ag···Ag separation across the*ortho* arms is shorter at 3.62 Å. This distance is also shorter than in the corresponding *ortho*-divinylbenzene complex with silver(I) perchlorate, which has a Ag···Ag separation of 4.43 Å. This is due to one of the vinyl groups, C4,C5 in Figure 4.10, twisting significantly out of the plane by a 20 ° angle. The Ag···Ag separation across the*para* vinyl arms is similar to **4.18** with two distances of 8.48 Å from Ag1 to Ag1A and 8.52 Å from Ag2 to Ag2C. The two different distances arise from the asymmetry in the conformation of the vinyl arms as C4,C5, as previously mentioned, is significantly twisted out of the plane. The shorter distance is across the two twisted vinyl arms.

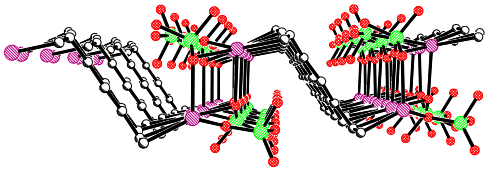
The overall structure of **4.19** is a two-dimensional sheet comprised of one-dimensional chains of silver(I) perchlorate, Figure 4.11(a), that are bridged together by ligand **4.10**, Figure 4.11(b). The silver(I) perchlorate chains are comprised of silver atoms of type Ag1 which is triply bridged to Ag2 by ligand **4.10**, a perchlorate through the same oxygen atom and a second perchlorate through two different oxygen atoms. These triple bridged units are linked together by Ag_2O_2 units which have either Ag1 or Ag2 type silver atoms. The two-dimensional sheet, like the previous complexes, is not flat but is buckled as can be seen in Figure 4.11(c). The sheets stack directly above and below each other with weak pseudo-doubly bridging perchlorate anions, see Figure 4.12, linking the two-dimensional sheets. Weak hydrogen bonding between perchlorate oxygen atoms and hydrogen atoms on ligand **4.10** (2.42 - 2.50 Å) are also present.



a)



b)



c)

Figure 4.11 *– **a)** One-dimensional chains of silver(I) perchlorate **b)** ligand **4.10** connecting silver(I) perchlorate chains to form a two-dimensional coordination polymer **c)** side view of the two-dimensional sheet showing the zig-zag nature. Hydrogen atoms have been excluded for clarity.*

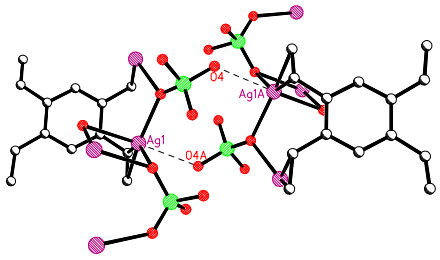


Figure 4.12 *- Weak pseudo-doubly bridging perchlorate anions linking two-dimensional sheets. Ag1···O4A 2.830(1) Å.*

With silver(I) tetrafluoroborate (**4.20**)

When reacted with silver(I) tetrafluoroborate, ligand **4.10** yields crystals that were analysed by X-ray diffraction. The data collected was poor at best and the structure solved in the space group Pnma but additional symmetry elements may be present. The counter anions were not refinable and there was additional unassigned electron density. Only the core structure, ligand **4.10** and the silver atoms were resolved and are shown in Figure 4.13. The collection was repeated with fresh crystals but yielded similar results.

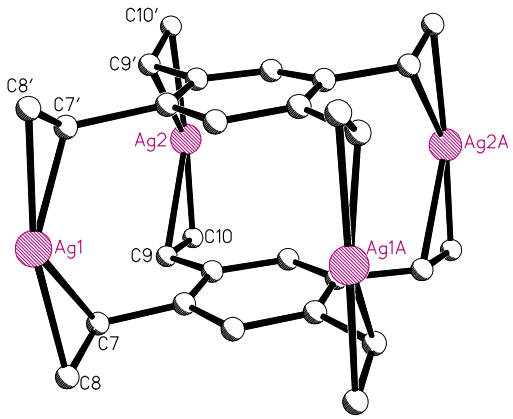


Figure 4.13 *– Core structure of complex* ***4.20****.*

The silver atoms are likely to be three coordinate with two alkenes and what appears to be an additional water molecule. It is expected that the Ag···Ag separation for the vinyl arms in the *ortho* and *para* relationships will be comparable to the distances in the related *ortho*- and *para*-divinylbenzene silver(I) complexes as the conformations are similar. The Ag···Ag separation across the *meta* vinyl arms would be similar to those in **4.18**. In this complex the ligand interacts with silver in a manner analogous to **1.28** in **2.10** in that it forms a discrete [4+2] macrocyclic cage and has all four silver atoms coordinated on the same side of the ligand.

4.5 Complexes of Tetraallylbenzene

With Silver(I) Triflate (**4.21**)

With the addition of an extra carbon in each of the arms in ligand **4.11** the flexibility is increased with respect to ligands **4.7** and **4.10** and they can now potentially adopt any number of solid state conformations. With the increase of flexibility the possibility of asymmetry of the solid state of ligand **4.11** is increased. This proved true for the case of **4.11** and silver(I) triflate. The structure solved in the space group P2/n with half a molecule of **4.11**, two silver atoms and two triflate counter anions in the asymmetric unit as shown in Figure 4.14.

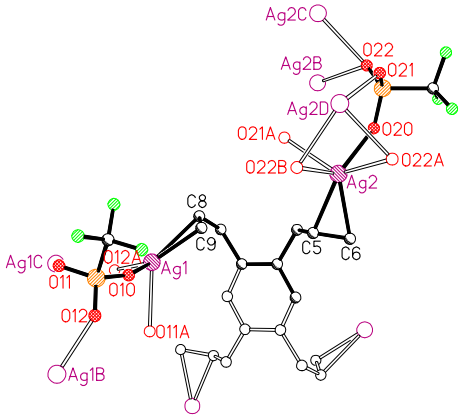
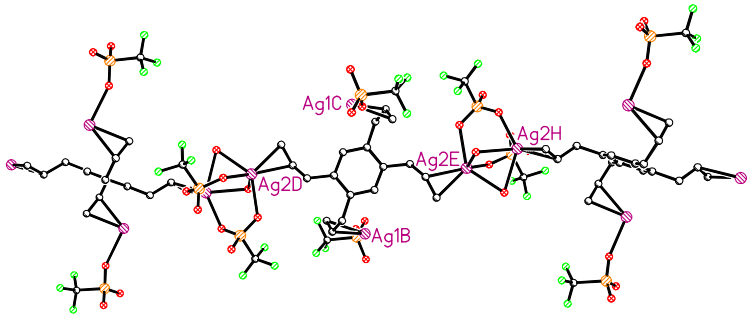
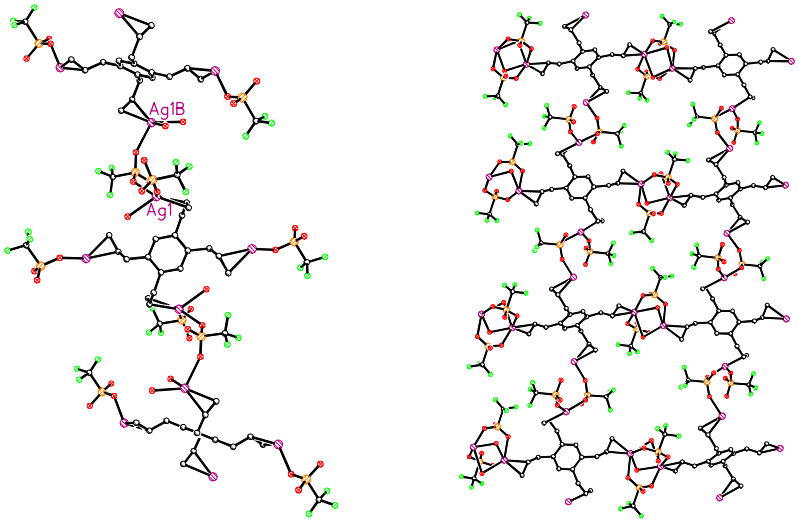


Figure 4.14 *– Contents of the asymmetric unit of* ***4.21****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C8 2.42(1), Ag1-C9 2.36(1), Ag1-C8,C9 2.29(1), Ag2-C5 2.36(1), Ag2-C6 2.35(1), Ag2-C5,C6 2.25(1), Ag1-O10 2.460(8), Ag1-O11A 2.487(9), Ag1-O12A 2.331(9), Ag2-C5 2.36(1), Ag2-C6 2.34(1), Ag2-C5,C6 2.25(1), Ag2-O20 2.344(9), Ag2-O21A 2.47(1), Ag2-O22A 2.550(9), Ag2-O22B 2.580(9), O10-Ag1-O11A 80.2(3), O10-Ag1-O12A 121.3(3), O11A-Ag1-O12A 81.0(3), O10-Ag1-C8,C9 102.2(4), O11A-Ag1-C8,C9 131.0(4), O12A-Ag1-C8,C9 147.4(4), O20-Ag2-O21A 84.0(3), O20-Ag2-O22A 79.1(3), O20-Ag2-O22B 129.4(3), O21A-Ag2-O22A 133.1(3), O21A-Ag2-O22B 79.7(3), O22A-Ag2-O22B 78.1(4), O20-Ag2-C5,C6 128.1(5), O21A-Ag2-C5,C6 109.9(4), O22A-Ag2-C5,C6 115.0(4), O22B-Ag2-C5,C6 102.5(5).*

There are two crystallographically independent silver atoms within **4.21**, Ag1 and Ag2, as shown in Figure 4.14. Ag1 is four coordinate with only one alkene coordinated, as in **4.19** with an additional three oxygen atoms from three separate triflate anions. Also as in **4.19**, the silver to C=C centroid distance is shorter at 2.29 Å. Ag1 has a calculated τ_4 value of 0.58 and has a see-saw geometry. Ag2 is five coordinate, only the second to arise within this work, with one alkene coordinated in addition to four oxygen atoms from four separate counter anions. It has distorted square pyramidal geometry. Again the silver to C=C centroid distance is short at 2.25 Å.



a)



b) ***c)***

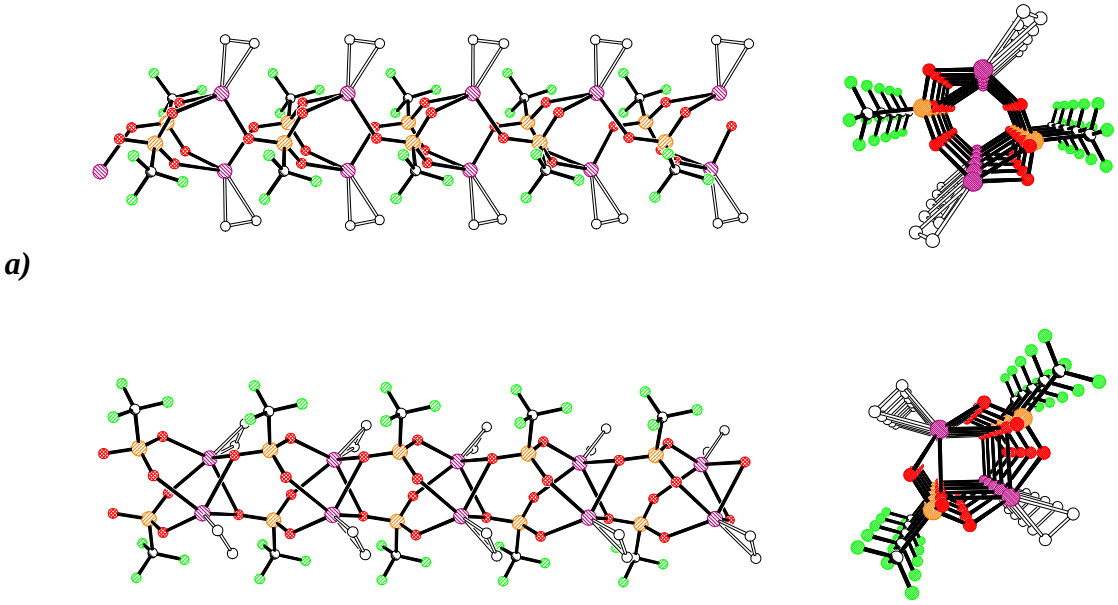
Figure 4.15 *– Building up the two dimensions of complex* ***4.21****. Hydrogen atoms have been omitted for clarity.* ***a)*** *One mode of polymer generation* ***b)*** *second mode of polymer generation* ***c)*** *two-dimensional sheet.*

Ligand **4.11** acts in a tetradentate fashion with all four allyl arms coordinated to silver. It lies on a centre of inversion and there are two pairs of allyl arms that are related by symmetry rather than all four as in **4.18**. As a result of the reduced symmetry in the conformation of the allyl arms the Ag···Ag separation across the two sets of allyl arms in a *para* relationship is no longer the same. There is a significant difference between the two *para* Ag···Ag separations with one, Ag1C and Ag1B in Figure 4.15(a), at 8.76 Å and the other, Ag2D and Ag2E, at 11.96 Å. The *ortho*, Ag1C and Ag2E, and *meta*, Ag1C and Ag2D, are very similar at 7.55 and 7.27 Å respectively. Additionally the Ag···Ag distance between quadruply bridged silver atoms, Ag2E and Ag2H figure 4.15(a), is very short at 3.19 Å and there is a slightly longer distance between singly bridged silver atoms, Ag1 and Ag1B in Figure 4.15(b), at 3.44 Å.

Complex **4.21** is comprised of two-dimensional square grids joined together in the third dimension by two different types of one-dimensional silver(I) triflate fragments. One direction of the two-dimensional grid is comprised of silver atoms that are alternatively bridged by ligand **4.11** through two allyl arms in a *para* relationship and then are quadruply bridged by triflate anions as seen in Figure 4.15(a). Within the quadruple bridge two triflate anions bridge through two different oxygen atoms and two bridge through the same oxygen atom. The second direction of grid consists of silver atoms that are alternatively bridged by ligand **4.11**, this time through a different pair of *para* allyl arms, and then singly bridged by a triflate anion as seen in Figure 4.15(b). Shown in Figure 4.15(c) is the overall two-dimensional sheet created by the interactions between silver(I), ligand **4.11** and triflate anions. In this instance the silver(I) triflate acts as the linear component and ligand **4.11** acts as the four connecting node which gives the two-dimensional square grid. While it appears there are one-dimensional pores running through the network, in reality there is very little void space as it is almost completely filled with fluorine atoms from the triflate anions.

The two-dimensional grids stack directly on top of one another and are linked together by two different types of one-dimensional silver(I) triflate chains. The first type of chain, shown in Figure 4.16(a), contains only silver atoms of the type Ag1. Each oxygen atom

on the triflate coordinates to different silver atoms and each silver atom is coordinated to three oxygens from different anions. Each silver atom is connected to five other silver atoms through bridging triflate anions. The second type of chain, shown in Figure 4.16(b), contains only silver atoms of type Ag2. In this silver(I) triflate chain, each triflate anion is coordinated to four silver atoms, through two singly coordinated oxygen atoms and one doubly coordinated oxygen atom. In turn each silver atom is coordinated to four oxygen atoms from four different triflate anions which results in one silver atom connecting to five others by bridging triflate anions. This second silver(I) triflate motif is also seen in a silver(I) triflate-benzene complex.[34]



a)

b)

Figure 4.16 *–* ***a)*** *One-dimensional silver(I) triflate chain formed with Ag1 silver atoms* ***b)*** *one-dimensional silver(I) triflate chain formed with Ag2 silver atoms.*

There are also additional weaker interactions within the structure which include offset π-π stacking between the benzene rings of ligand **4.11**.

4.6 Complexes of Tetraallylbenzoquinone

With silver(I) hexafluorophosphate (**4.22**)

The intermediate quinone **4.13**, in the synthetic pathway to **4.14**, is itself a potential ligand and was reacted with a range of silver(I) salts in a silver(I) to ligand ratio of 2:1. Ligand **4.13** is similar to **4.11** but has the additional oxygen atoms at the 1,4 positions which may constrain some of the freedom of the allyl arms through steric hindrance. The reaction of **4.13** with silver(I) proved successful for silver(I) hexafluorophosphate **4.22** and silver(I) triflate (**4.23**), both giving yellow crystalline solids and were suitable for single crystal X-ray analysis. Complex **4.22** solved in the space group P-1 with half a molecule of **4.13**, one silver atom, one hexafluorophosphate counter anion and a coordinated solvent molecule in the asymmetric unit as shown in Figure 4.17.

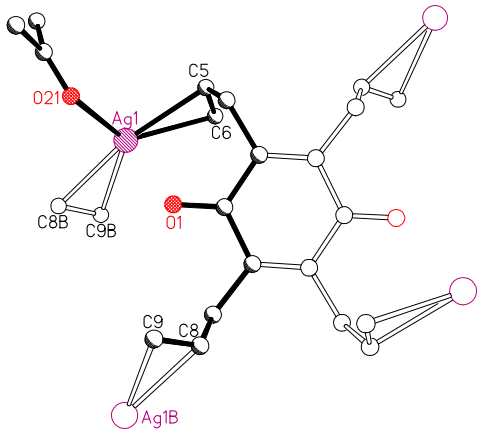


Figure 4.17 *– Asymmetric unit of complex* ***4.22****. Hydrogen atoms and counter anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C5 2.422(5), Ag1-C6 2.422(5), Ag1-C5,C6 2.328(5), Ag1-C8 2.427(5), Ag1-C9 2.350(6), 2.301(6), Ag1-O21 2.287(3), O21-Ag1-C5,C6 109.1(2), O21-Ag1-C8,C9 108.4(2), C5,C6-Ag1-C8,C9 141.9(2).*

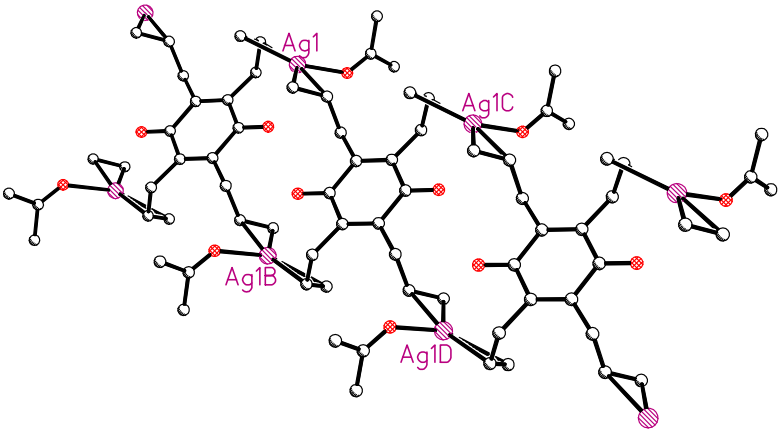
Within complex **4.22** each silver atom is three coordinate with two alkenes and a carbonyl oxygen from an acetone molecule coordinated. Its geometry is between T-shaped and trigonal planar with the largest angle, 142 °, between the two coordinated

alkenes. The carbonyl oxygens in **4.13**, O1, also weakly interact with Ag1 with a distance of 2.68 Å.

Ligand **4.13** lies on a centre of inversion with only half a molecule in the asymmetric unit. It is tetradentate and bridges four silver atoms through the coordination of all four alkenes. The allyl arms are, starting from a carbonyl oxygen, in an up, up, down, down conformation. The silver atoms are bridged by ligand **4.13** in four ways; through the allyl arms in either an *ortho* or *meta* relationship or in two different *para* relationships. The Ag···Ag separations across ligand**4.13** is as follows; *ortho*, Ag1···Ag1C in Figure 4.18(a), 8.18 Å, *meta* Ag1···Ag1B 7.01 Å, *para*1 Ag1···Ag1D 12.03 Å and *para*2 Ag1B···Ag1C 9.31 Å. One of the para conformations has a much shorter Ag···Ag separation, as both allyl arms curl back towards the carbonyl oxygen atom to enable it to weakly interact with the coordinated silver atom. The curling back of two of the arms also results in the distance across the *meta* separation being shorter than across the *ortho*. The longer distance across the *para* allyl arms is very similar to those in, **2.12** and **2.13**, the related *para*-diallylbenzene silver(I) complex.

The change from a benzene core in **4.11** to a quinone core in **4.13** leads to significant structural changes. Ligand **4.13** now forms a one-dimensional metallopolymer with silver(I), shown in Figure 4.18(a), as opposed to a three-dimensional polymer in **4.21**. The new polymer, similar to **3.17**, can be classed as a necklace polymer as the ligand acts as a four connecting node and the silver as the angular component as shown in Figure 4.18(b). Non-bridging acetone molecules cap the third coordination site on the silver.

One-dimensional polymers stack in an ABCA manner. The hexafluorophosphate counter anions sit between the capping acetone molecule with weak hydrogen bonding between hydrogen atoms on the acetone and fluorine atoms on the counter anion (2.37 - 2.57 Å). The anions also sit above acetone molecules and approximately below a benzene ring from different polymer chains with further weak hydrogen bonding (2.54 Å) providing stability for the three-dimensional structure.



a)

b)

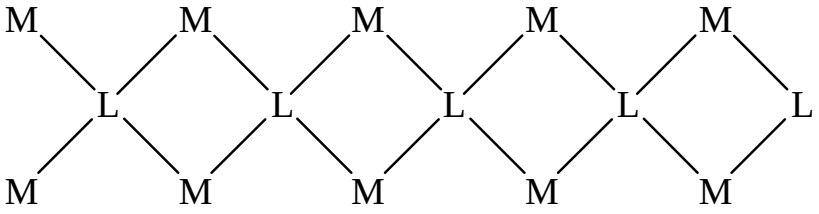


Figure 4.18 *– View of the one-dimensional metallopolymer. Hydrogen atoms and counter anions have been omitted for clarity.* ***a)*** *The one-dimensional polymer* ***4.22*** ***b)*** *schematic of a necklace polymer, M=Ag*$^{+}$ *and L = ligand* ***4.13****.*

With silver(I) triflate (**4.23**)

The second complex with ligand **4.13** solved in the higher symmetry space group $P2_1/c$. The contents of the asymmetric unit, shown in Figure 4.19, are different to **4.22** in that there is no coordinated solvent molecule. However it has the same silver to ligand ratio, 2:1, with half a molecule of **4.13**, one silver atom and one triflate counter anion.

The silver atoms in **4.23** are now four coordinate, as opposed to three coordinate in **4.22**, with two alkenes and two oxygen atoms, from the counter anions, coordinated. The calculate τ_4 value for Ag1 is 0.81 indicating a trigonal pyramidal geometry. The carbonyl oxygen, O1, still has close proximity to silver, as in **4.22**, but is slightly further away at 2.79 Å. Again the greatest angle, 133 ° is between the two coordinated alkenes.

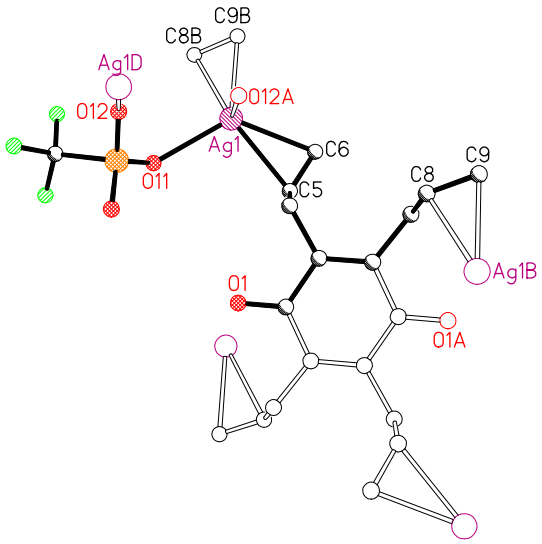
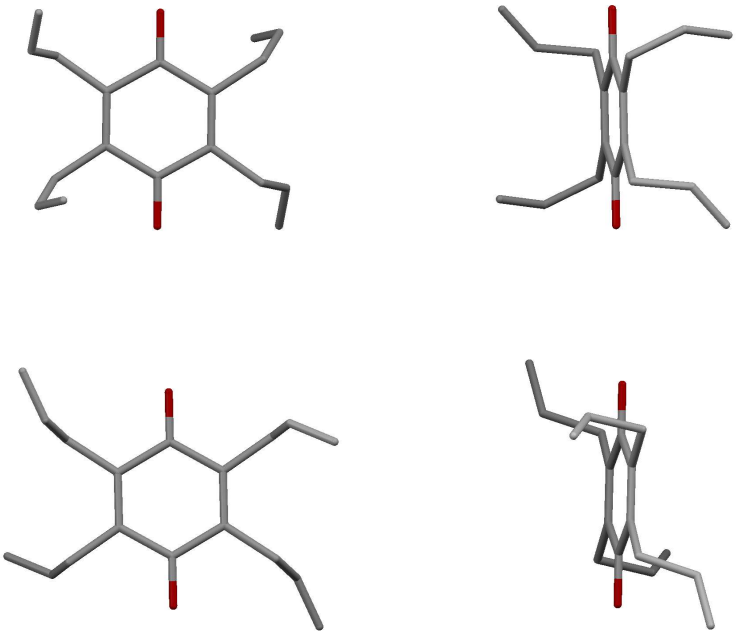


Figure 4.19 *– Asymmetric unit of complex* ***4.23****. Hydrogen atoms have been excluded for clarity. Selected bond lengths (Å) and angles (°): Ag1-C5 2.472(4), Ag1-C6 2.377(4), Ag1-C5,C6 2.331(4), Ag1-C8 2.455(4), Ag1-C9 2.414(4), Ag1-C8,C9 2.341(4), Ag1-O11 2.355(3), Ag1-O12 2.515(3), O11-Ag1-O12 93.6(1), O11-Ag1-C5,C6 113.1(1), O11-Ag1-C8,C9 108.5(1), O12-Ag1-C5,C6 88.6(1), O12-Ag1-C8,C9 109.3(1), C5,C6-Ag1-C8,C9 133.3(2).*

As in **4.22**, the ligand is tetradentate, bridging four silver atoms through the coordination of all four alkenes. Ligand **4.13**, as in the previous complex, lies on a centre of inversion with half a molecule in the asymmetric unit. The allyl arms have a different conformation than in **4.22** which are compared in Figure 4.20. Ligand **4.13** now has, starting at an oxygen atom, an up, down, down, up conformation.

As in **4.22**, the silver is bridged by ligand **4.13** in four ways with the Ag···Ag distances as follows: *ortho*, Ag1···Ag1D (Figure 4.21(a)), 8.56 Å, *meta* Ag1···Ag1M 6.11 Å, *para*1 Ag1···Ag1B 12.12 Å and *para*2 8.61 Å. The Ag···Ag separation is again shorter over the allyl arms in a *meta* relationship. There is a lot of variation in the Ag···Ag separations across the allyl arms between complexes **4.21**, **4.22** and **4.23** which is a reflection of the

flexible nature of the allyl arm. Two silver atoms, Ag1 and Ag1A, are also separated by doubly bridging triflate anions with a separation of 5.33 Å which is consistent with previous examples.[††]



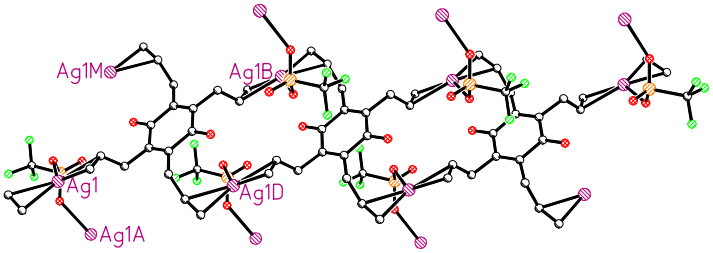
a)

b)

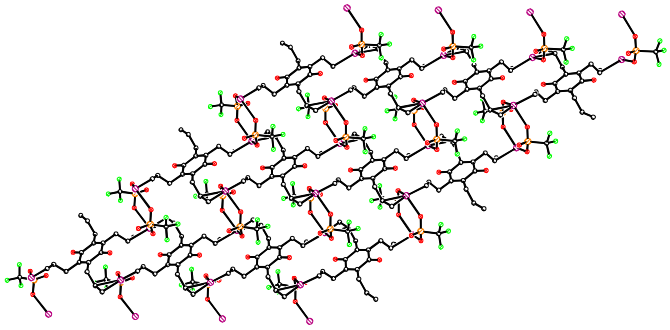
Figure 4.20 *– Comparison of the solid state conformation of ligand* ***4.13*** *in complexes* ***4.22*** *and* ***4.23****.* ***a)*** *View of the conformation of* ***4.13*** *in complex* ***4.22*** ***b)*** *view of the conformation of* ***4.13*** *in complex* ***4.23****.*

Again the structure is a necklace polymer, shown in Figure 4.21(a). However the capping acetone molecules are replaced by bridging triflate anions which gives rise to a two-dimensional sheet of linked necklaces. The necklaces are joined together by doubly bridging triflate anions as shown in Figure 4.21(b). There are no significant interactions between the two-dimensional sheets.

[††] Doubly bridging triflate anions are also seen in complexes **3.22** and **6.17**.



a)



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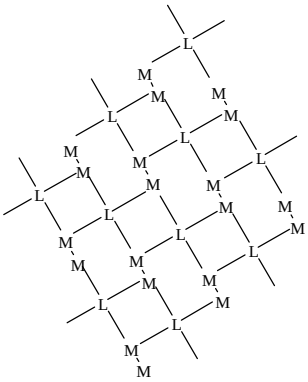


c)

Figure 4.21 *– Extended structure of* ***4.23****.* ***a)*** *Showing structural similarity to* ***4.22*** ***b)*** *showing a two-dimensional sheet of linked necklaces* ***c)*** *schematic of the overall two-dimensional network M-M = two silver atoms doubly bridged by triflate anions, L = ligand* ***4.13****.*

4.7 Complexes of 1,4-Di(allyloxy)-2,5-diallylbenzene

With silver(I) perchlorate (**4.24**)

In changing from ligand **4.11** to **4.12** two of the allyl arms are exchanged with two allyl ether arms. This causes a loss of symmetry with no possibility of symmetry between all four arms and it is an expected that the Ag···Ag distances across *para* allyl ether arms will be longer than across *para* allyl arms.

Ligand **4.24** was combined successfully with silver(I) perchlorate and its crystal structure solved in the space group $P2_1/c$. The asymmetric unit, shown in Figure 4.22, revealed a silver to ligand ratio of 2:1 containing half a molecule of **4.12**, one silver atom and counter anion as well as a coordinated acetone solvent molecule.

The silver is four coordinate with two alkenes and two oxygen atoms coordinated. The calculated τ_4 value for Ag1 is 0.78 indicating a see-saw type geometry with the largest angle between the two alkenes and the smallest between the two oxygen atoms. Ligand **4.12** bridges four silver atoms and has all four alkenes coordinated. It lies on a centre of inversion which results in each of the two types of arms i.e. both the allyl and both the allyl ether arms having symmetry related conformations.

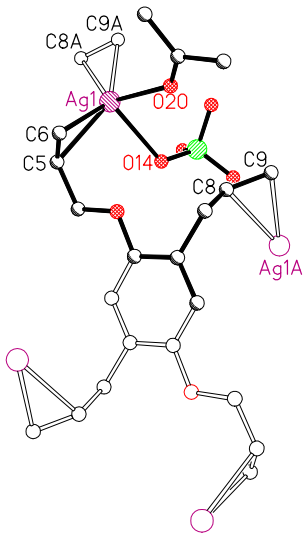
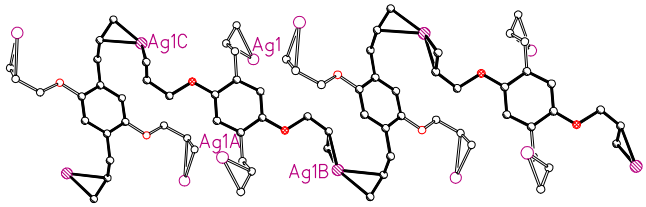


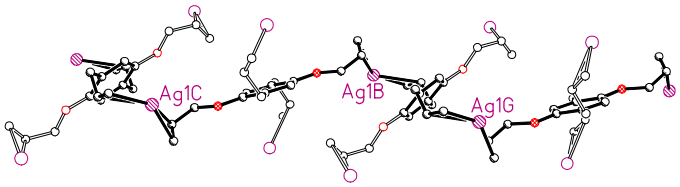
Figure 4.22 *– Asymmetric unit of complex* ***4.24****. Hydrogen atoms and disorder have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C5 2.465(4), Ag1-C6 2.353(5), Ag1-C5,C6 2.341(5), Ag1-C8A 2.501(3), Ag1-C9A 2.353(3), Ag1-C8A,C9A 2.333(3), Ag1-O14 2.528(2), Ag1-O20 2.362(3), O14-Ag1-O20 86.21(8), O14-Ag1-C5,C6 110.8(2), O14-Ag1-C8A,C9A 107.3(1), O20-Ag1-C5,C6 101.5(2), O20-Ag1-C8A,C9A 116.9(1), C5,C6-Ag1-C8A,C9A 133.1(2).*

Ligand **4.12** bridges two silver atoms in four different ways. The first two ways is for it to bridge through either two allyl arms or two allyl ether arms. The other two ways is for it to bridge two silver atoms by an allyl arm and an allyl ether arm in either a 1,2 or a 1,3 relationship. The Ag···Ag separation across both the allyl arms, Ag1···Ag1A in Figure

4.23(a), is 8.55 Å and across both the allyl ether arms, Ag1B···Ag1C, is 12.51 Å. These values are in line with previous distances across *para* allyl ether arms and the distance across the *para* allyl ether arms is the longest in this work. The Ag···Ag separation across both an allyl and an allyl ether arm in the 1,2 relationship, Ag1···Ag1C, is 6.50 Å and the 1,3 relationship, Ag1···Ag1B, is longer at 8.53 Å.This is respectively shorter and longer than the analogous allyl arms in **4.21**, **4.22** and **4.23**.



a)



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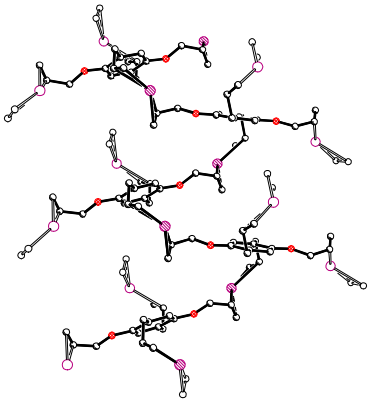
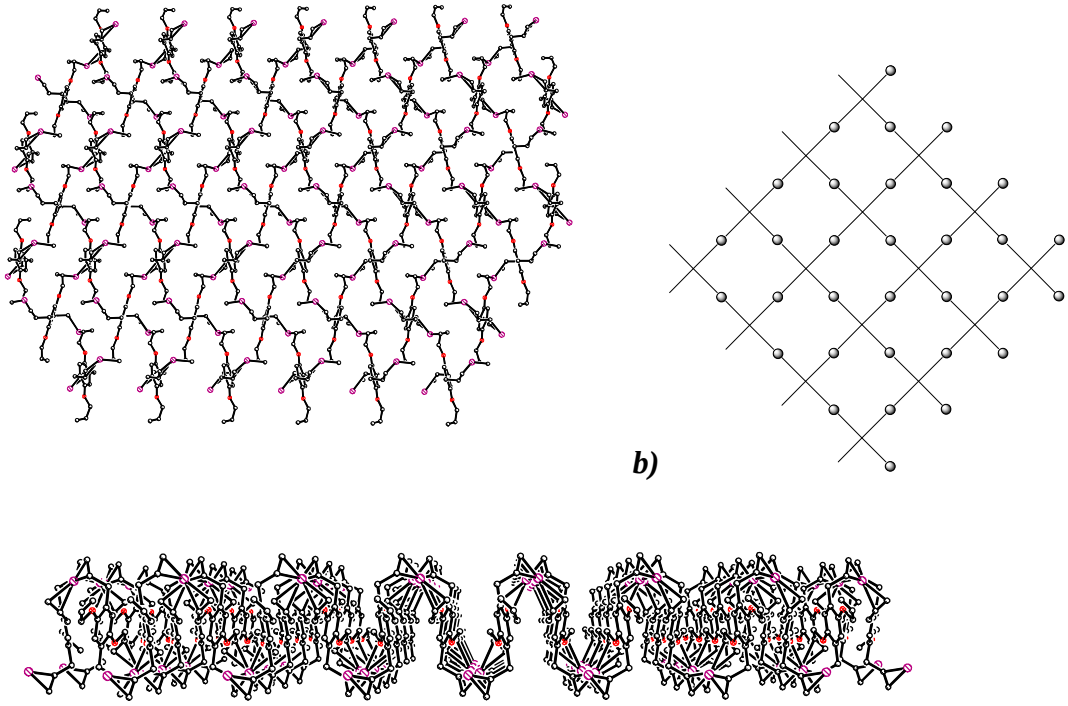


c)

Figure 4.23 *– Buliding up the two-dimensional structure of* ***4.24****.* ***a)*** *Silver atoms bridged by alternating between two allyl arms and then two allyl ether arms* ***b)*** *different view point of a)* ***c)*** *silver atoms bridged by an allyl arm and an allyl ether arm in a 1,3 relationship.*

Both the coordinated counter anion and acetone solvent molecule are non-bridging and do not contribute to the framework of the structure, which is made up of ligand **4.12** and silver. The structure is a two-dimensional metallopolymer where one dimension of the polymer is made up of silver atoms alternately bridged by two allyl ether arms then two allyl arms as seen in Figure 4.23(a,b). The second dimension consists of silver being bridged through an allyl ether arm then an allyl arm in a 1,3 relationship which is shown in Figure 4.23(c).



a) ***b)***

c)

Figure 4.24 *– Overall structure of* ***4.24****.* ***a)*** *View of the two-dimensional distorted square grid* ***b)*** *schematic of a two-dimensional squared grid where the spheres represent a metal ion and the lines a four connecting ligand* ***c)*** *side view showing the undulation of the grid.*

The metallopolymer is a two-dimensional square grid, shown in Figure 4.24(a), where ligand **4.24** is the four connecting unit and the silver is the linear unit. Ligand **4.24** does not have exactly 90 ° angles and the silver is not completely linear so the grid is distorted. It is also not flat and undulates when viewed from the side, as in Figure 4.24(c). The two-

dimensional grids are stacked directly upon each other in a manner that results in one-dimensional pores that run through the structure. These pores have approximate dimensions of 7.6 Å × 7.6 Å, measured between the centroid of the benzene rings in **4.12**. The pores are filled by coordinated perchlorate anions and acetone molecules from the grid.

With silver(I) hexafluorophosphate (**4.25**)

Success was also achieved from the reaction of ligand **4.12** and silver(I) hexafluorophosphate, yielding crystals suitable for X-ray diffraction. The structure solved in the space group $P2_1/n$ and the asymmetric unit, shown in Figure 4.25, again showed a 2:1 silver to ligand ratio containing half a molecule of **4.12**, one silver atom and one hexafluorophosphate counter anion as well as a coordinated acetone molecule.

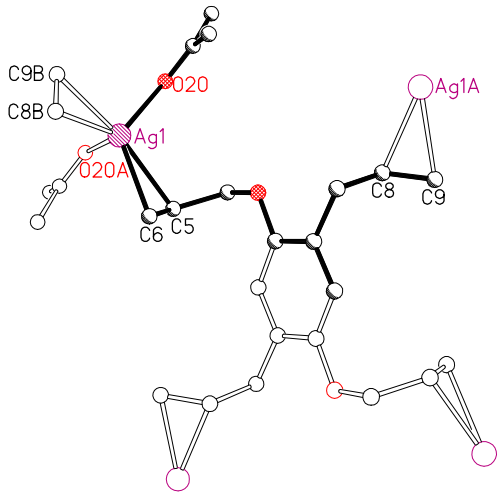


Figure 4.25 *– Asymmetric unit of complex* ***4.25****. Hydrogen atoms and counter anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C5 2.402(4), Ag1-C6 2.369(4), Ag1-C5,C6 2.291(4), Ag1-C8B 2.392(4), Ag1-C9B 2.335(4), Ag1-C8B,C9B 2.269(4), Ag1-O20 2.380(2), Ag1-O20A 2.569(3), O20-Ag1-O20A 76.25(9), O20-Ag1-C5,C6 110.7(1), O20-Ag1-C8B,C9B 113.3(1), O20A-Ag1-C5,C6 97.8(1), O20A-Ag1-C8B,C9B 109.3(1), C5,C6-Ag1-C8B,C9B 131.6(2).*

As in **4.24**, the silver atoms are four coordinate with two olefins and two oxygen atoms coordinated. As hexafluorophosphate is a non-coordinating anion the second oxygen is supplied by a second molecule of coordinated acetone. Silver atoms have a calculate τ_4 value of 0.82 indicating a slightly more trigonal pyramidal geometry than **4.24**. Similar to **4.24** the largest angle is between the two olefins and the smallest is between the two oxygen atoms. Ligand **4.12** lies over a centre of inversion also similar to **4.24**.

The four arms in **4.25** are in a more stretched conformation than in **4.24** with, in general, longer Ag···Ag separations. The Ag···Ag separationacross both allyl arms, Ag1A and Ag11C in Figure 4.26(a), is 11.62 Å and across both allyl ether arms, Ag1 and Ag1B, is 12.34 Å. The separation across both an allyl and an allyl ether arm in a 1,2 relationship, Ag1B and Ag1C, is 8.03 Å and a 1,3 relationship, Ag1A and Ag1B, is 9.06 Å.

The replacement of a coordinated perchlorate anion in **4.24** by a second coordinated acetone molecule as well as a larger anion gives rise to a completely different architecture. The overall structure has changed from a two-dimensional distorted grid as in **4.24** to a three-dimensional metallopolymer with much simpler connectivity. The polymer can be considered as three one-dimensional polymers that are connected together to form the whole. Two of the one-dimensional polymers are the same and the third is different with two different orientations within the three-dimensional structure. The first polymer consists of silver atoms that are bridged solely by the two allyl ether arms in ligand **4.12** which is then alternated with doubly bridging acetone molecules as shown in Figure 4.26(a). This is the unique one-dimensional polymer and it has two different orientations which are perpendicular with respect to each other as shown in Figure 4.26(a) and (b). These different orientations of the strand alternate in an ABA manner so that every second strand is in the same orientation. The second type of one-dimensional polymer is comprised of silver atoms that are bridged by only the allyl arms in ligand **4.12** and then doubly bridged acetone molecules as shown in Figure 4.26(c). As a consequence of the two different orientations of the first polymer the allyl arms point in two directions which results in the second type accounting for two dimensions of the three-dimensional network.

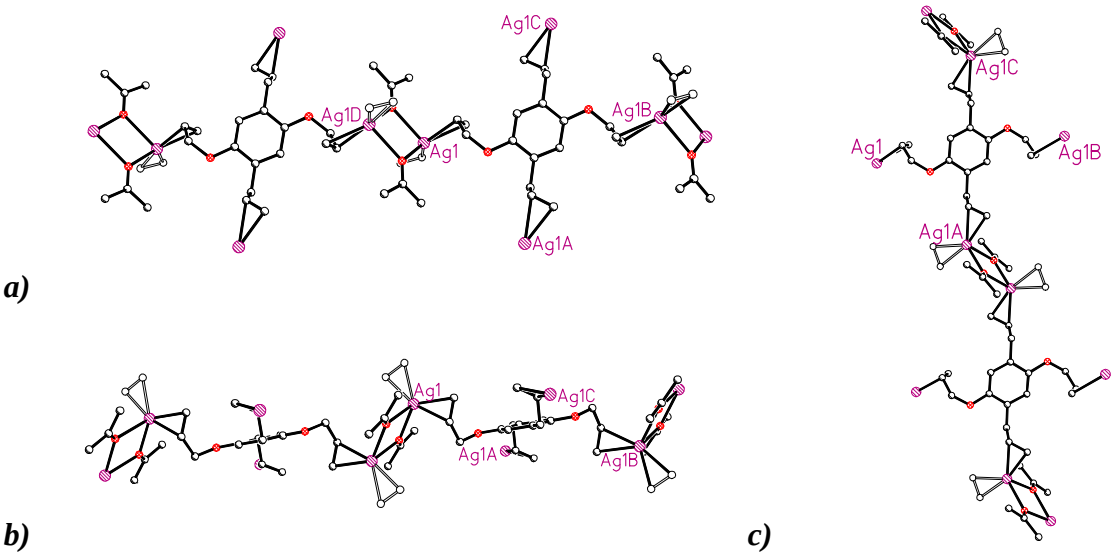


Figure 4.26 *– Generation of the three dimensions of* ***4.25****.* ***a)*** *Bridging of silver atoms by alternating allyl ether arms in ligand* ***4.12*** *and acetone solvent molecules* ***b)*** *second orientation of a)* ***c)*** *bridging of silver atoms by alternating allyl arms in* ***4.12*** *and acetone solvent molecules.*

The three-dimensional network is porous with voids of approximate dimensions of 7.4 Å × 7.4 Å × 14.4 Å. The void space is filled with coordinated acetone molecules and hexafluorophosphate counter anions. The counter anions are held in place through multiple weak hydrogen bonding interactions between fluorine atoms and hydrogen atoms on the coordinated acetone and ligand **4.12** with distances ranging between 2.43 – 2.64 Å.

Ligand **4.12** forms two- and three-dimensional porous networks with silver(I) which is of great interest for applications such as gas purification, separation and storage, as well as catalysis.[146] Elemental analysis of **4.24** shows five out of every six acetone molecules are lost over time and in **4.25** it suggests that, over time, the acetone molecules are slowly being replaced by water molecules. However it is unlikely that these two compounds

would be useful for such applications as they have poor thermal stability. In compound **4.25**, the silver starts to decompose at 105 °C with the crystals blackening, and **4.24** undergoes explosive decomposition at 119 °C.

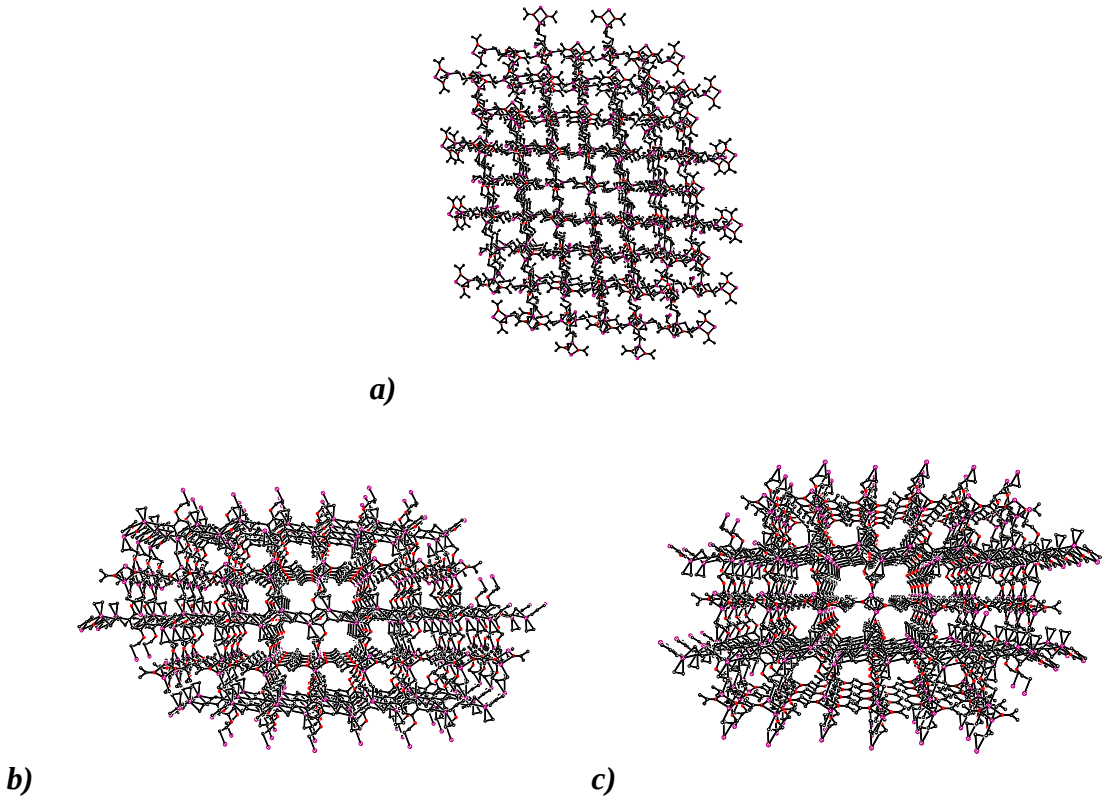


Figure 4.27 *– View of the porous network. Hydrogen atoms have been omitted for clarity.* ***a)*** *View of the unique side of the porous three-dimensional network* ***b)*** *view of the second side of the porous three-dimensional network* ***c)*** *view of the third side of the porous three-dimensional network which is the symmetry equivalent of b).*

SIX ARMED LIGANDS

4.8 Complexes of 1,2,4,5-Tetraallyl 3,6-di(allyloxy)benzene

With a very low yield of ligand **4.14** a proper investigation was not possible. This is an area for further investigation as other six armed ligands, such as hexavinyl- and

hexaallyl-benzene, might be synthesised in higher yields from Stille coupling with the hexabromobenzene precursor.

4.9 Summary

This chapter details the synthesis of three tri-armed, four tetra-armed and one hexa-armed ligand. They are based around a benzene core with the exception of **4.13** which has a benzoquinone core. Ligands have arms with varying degrees of flexibility to allow a range of assemblies to form. Ligands **4.8**, **4.11**, **4.13** and **4.14** are previously unknown. The coordination chemistry of these ligands with silver(I) was explored with a variety of salts including coordinating and non-coordinating counter anions. Nine new complexes were formed and studied by single crystal X-ray diffraction.

The formation of polymeric structures was strongly favoured with the formation of one-, two- and three-dimensional coordination polymers. Ligands **4.7** and **4.11** form one-dimensional coordination polymers with $AgClO_4$ and $AgPF_6$ respectively. Ligands **4.10**, **4.12** and **4.13** form two-dimensional networks with silver(I) and **4.10** forms two different networks with different ratios of ligand and silver(I). Three-dimensional networks arise from the combination of ligands **4.11** and **4.12** with $AgCF_3SO_3$ and $AgPF_6$ respectively. A common characteristic of the one- and two-dimensional polymers is that they are not flat and undulate or are zig-zagged. An additional common feature is that four armed ligands favoured the formation of complexes with a 2:1 silver to ligand ratio with the exception of **4.19**. Ligand **4.10** also forms a discrete [4+2] macrocyclic cage with $AgBF_4$.

There was a marked preference, in this chapter, for silver atoms to be four coordinate and to adopt distorted tetrahedral or trigonal pyramidal geometries. Commonly the silver is coordinated to two olefinic moieties and two oxygen atoms from various sources. The largest angle around the silver was generally between the two olefins and the smallest between the two oxygens. Less prevalently silver had one alkene and three oxygens coordinated to it. A rarer five coordinate silver was identified in **4.21**. In all cases where

there was only one olefin coordinated to a silver atom the distance between the C=C centroid and silver was shorter as occurred in complex **2.12**.

Vinylbenzenes give the greatest amount of predictability as their solid state conformations are partially restricted. Ligand **4.7** could adopt two potential solid state conformations and ligand **4.8** only one likely solid state conformation. Silver atoms can coordinate either on the same side or on opposing sides of the ligand relative to each other. *Ortho* vinyl arms can have either both silver atoms on the same side or on opposite sides and both of these conformations were identified. This gave Ag···Ag separations of 6.81 Å and 3.62 Å respectively. *Meta* vinyl arms have a total of six different possible conformations that silver atoms could coordinate, of which four were identified. The most common was the silver atoms coordinating to the same side of the molecule and the vinyl arms pointing towards each other. This conformation consistently gives a Ag···Ag separation of ~5.6 Å. The other conformations were silver on opposing sides with both of the vinyl arms pointing away from each other as well as one pointing towards and one pointing away giving Ag···Ag separations, of 8.01 Å and 8.47 Å, respectively. The last conformation identified was both vinyl arms pointing towards each other with the silver atoms coordinated on opposing sides of the ligand which has an Ag···Ag separation of 7.69 Å. Vinyl arms in a *para* relationship have four possible conformations of silver coordination although only two were identified with the vinyl groups pointing in opposite directions and silver coordinated on either the same side or opposite sides of the ligand. The Ag···Ag separations had a small range with an average of 8.5 Å In general there was some variation in all of the distances as the vinyl arms occasionally lie out of the plane of the benzene with the largest example at an angle of 20 ° in **4.19**.

Allyl and allyl ether solid state conformations are much harder to define as there is more freedom with the additional atoms and the rotation is not restricted as in the vinylbenzenes. A range of Ag···Ag separations were recorded across two allyl arms in either an *ortho*-, *meta*- and *para*- relationship and is summarised in Table 4.1. The *para* relationship showed the greatest range of 3.5 Å, however this was the biggest sample

group and the larger range may be a reflection of that. *Para* allyl ether arms give Ag···Ag separations between 10.62 – 12.51 Å with an approximate range of 2 Å.

Relationship	Shortest (Å)	Longest (Å)	Approx. Range (Å)
Ortho	7.55	8.56	1.0
Meta	6.11	7.27	1.2
Para	8.55	12.02	3.5

Table 4.1 *– Summary of the Ag···Ag separations across allyl arms in an ortho-, meta- and para- relationship.*

Chapter Five

Ligands with Non-Aromatic Cores

CHAPTER 5

Ligands with Non-Aromatic Cores

5.1 Introduction

The previous chapters describe ligands with aromatic cores, such as benzene in chapters two and four, and naphthalene in chapter three. The aromatic core gives rigidity and preorganisation to the ligand and also provides weak interactions such as π-π stacking that can give order and stability to the overall three-dimensional architecture. This enhances the likelihood of producing a single crystalline product. This chapter will investigate whether ligands without any aromatic moieties will have success in producing similar architectures involving silver(I)-alkene interactions.

A range of core geometries and number of binding domains can arise from using different atom types at the centre of a ligand as shown in Figure 5.1. For example, an oxygen atom can give a two armed ligand with a bent core geometry, a nitrogen atom at the core can give a three armed ligand and will have trigonal pyramidal geometry and using a carbon atom as a core can give rise to four armed ligands with tetrahedral geometry. The atom type is not limited to these examples and other heteroatoms such as sulfur and silicon can be used.

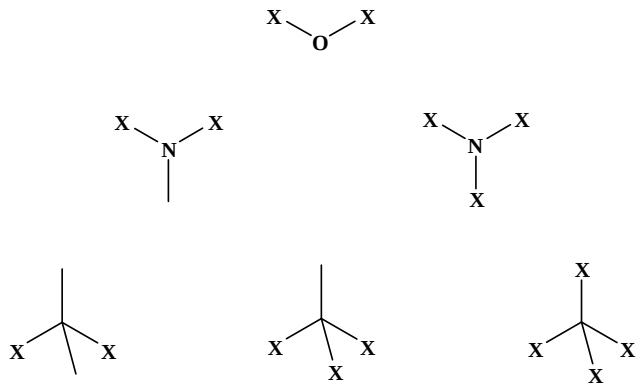


Figure 5.1 *– Some examples of various geometries and denticities available with simple single atom cores. X denotes a metal binding functional group.*

There are many examples of bridging ligands with non-aromatic cores which have been used in metallosupramolecular chemistry. However, it is rare that a ligand contains no aromatic moiety at all, as aromatic nitrogen heterocycles are commonly used as functional groups to bind to the metal. To have a ligand without aromaticity the pool of possible functional groups is greatly reduced but still includes carboxylic acids, alcohols, ethers, amines and alkenes. There are few reports of silver(I) complexes with these types of ligand,[147,148] however closely related work with the copper(I)-alkene synthon has been exploited to form a range of architectures with ligands, such as those in Figure 5.2, which contain no aromatic moieties. Much of this work has been published by Russian scientists in rather obscure journals.

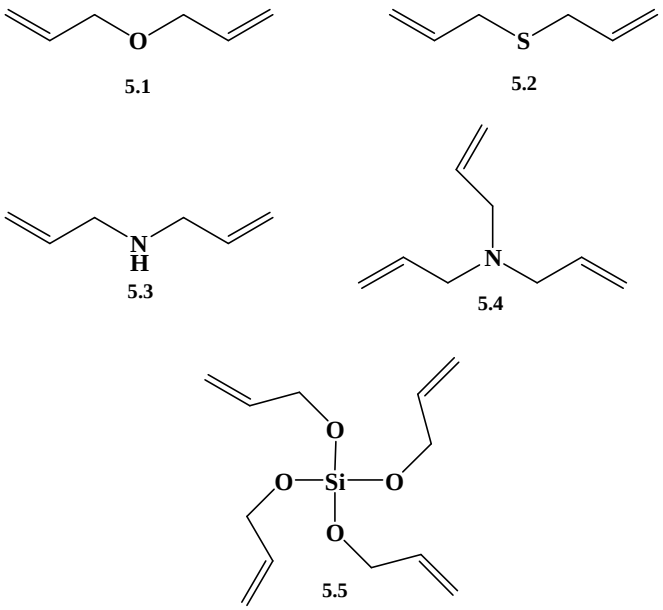


Figure 5.2 *– Examples of non-aromatic ligands previously used in combination with either silver(I), copper(I) or both.*

There are four examples of complexes of copper(I) and diallyl ether (**5.1**), three of which are with CuCl and the fourth is with CuO_3SCH_3. Two of the compounds of **5.1** with CuCl are polymorphs with the formula 2CuCl.**5.1**. The first polymorph was identified by Fundamenskii et al.[149] in 1986 and has continuous chains of (-Cu-Cl-)n which are linked together into a two-dimensional network by bridging molecules of **5.1**. Weak associations

between copper and chlorine atoms of different chains link the two-dimensional networks into the third dimension. The second polymorph was reported by Olijnyk et al.[150] in 2008. The major difference in the second polymorph lies in the inorganic CuCl construction. The second polymorph has two crystallographically independent Cu_2Cl_2 units which are linked together by bridging molecules of **5.1** to give a one-dimensional polymer. As in the first polymorph, weak associations between copper and chlorine atoms link the one-dimensional polymers into the second dimension. The third complex of **5.1** with copper(I) chloride has a higher ratio of copper with a empirical formula of 5CuCl.**5.1**.[151] This complex is also a one-dimensional polymer with ligand **5.1** doubly bridging Cu_5Cl_5 clusters. The clusters themselves are linked together, as in the two previous examples, through weak copper-chlorine interactions.

The last example of **5.1** with Cu(I) was reported by Pan et al.[152] in 2006 where CuCl underwent ion exchange with silver(I) methanesulfonate. X-ray analysis on the new compound revealed it to be tetranuclear, as shown in Figure 5.3.

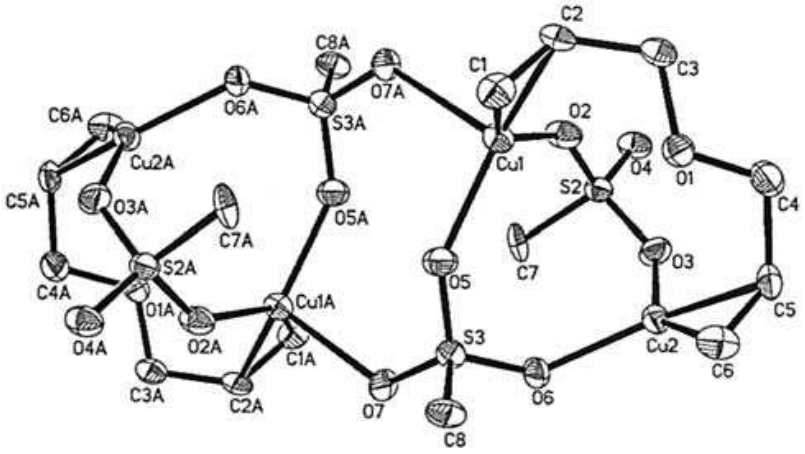


Figure 5.3 *– View of the copper(I) methansulfonate tetranuclear complex with* ***5.1****.*[152]

Each monomer unit has two symmetrically independent copper atoms that are bridged by ligand **5.1** and two sulfonate groups, one of which further bridges to another such unit about a centre of inversion.

Ligand **5.1** has also been used in combination with Pt(0)[153], Pd(0)[153-155] and Ni(0)[156]. A palladium(0) complex with **5.1** was isolated and characterised by X-ray crystallography by Pörschke et al.[153] and revealed a simple discrete structure shown in Figure 5.4. The central palladium is three coordinate with trigonal planar geometry. It has a trimethylphosphine molecule coordinated through the phosphorous atom and ligand **5.1** chelates to the palladium atom through both carbon-carbon double bonds.

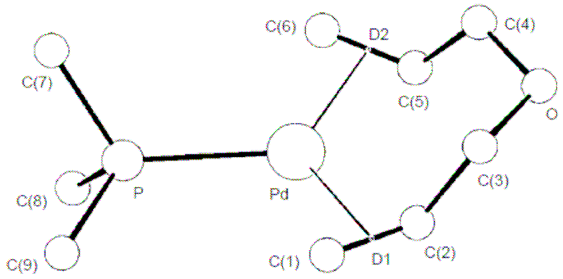


Figure 5.4 *– View of* ***5.1*** *chelating to Palladium(0).*[153]

By changing the core atom from oxygen in ligand **5.1** to sulfur in diallyl sulfide (**5.2**) different structures arise. This is due to an increase in the different modes of ligand bonding since **5.2** can act as a bi-functional ligand with the sulfur atom acting as a donor to copper(I). Four different binding modes of **5.2** have been seen in the literature and are summarised in Figure 5.5.

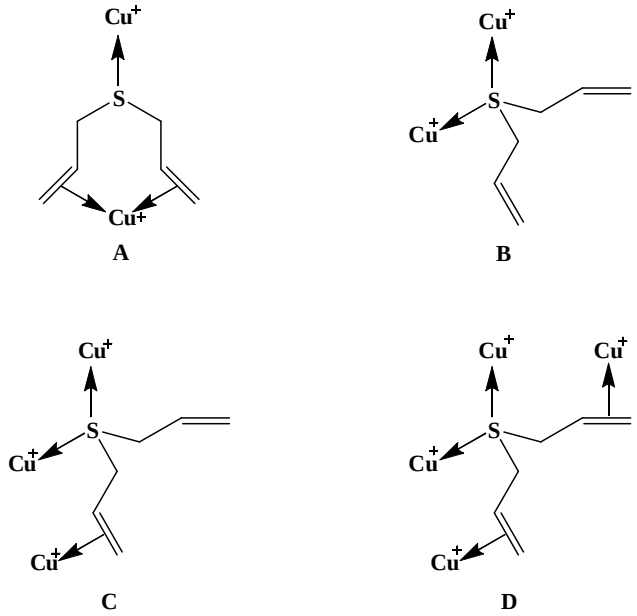


Figure 5.5 *– The four binding modes of* ***5.2*** *to copper(I).*[157-159]

Binding mode A has **5.2** acting as a tridentate ligand and occurs when **5.2** is combined with copper(I) tetrafluoroborate which results in a one-dimensional metallopolymer.[157] Additionally if **5.2** is combined with silver(I) perchlorate it will also adopt this binding motif and result in a one-dimensional metallopolymer.[147] Both binding modes B and D occur within the product resulting from the reaction of copper(I) chloride and **5.2** giving an overall two-dimensional structure.[158] Finally, binding mode C occurs when **5.2** is reacted with copper(I) bromide and gives a one-dimensional metallopolymer.[159]

As in **5.2**, the nitrogen atom at the core of diallyl amine (**5.3**) can also act as donor to copper(I) but in a different manner to the sulfur atom which gives rise to further structural variation. Figure 5.6 shows the binding modes of **5.3** with copper(I) found in the literature. Note that only one mode is shared between both **5.2** and **5.3**.

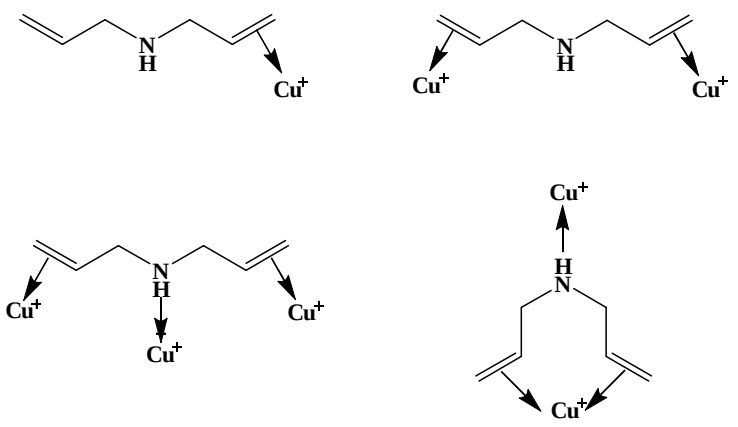


***Figure 5.6** – Known binding modes of **5.3** with copper(I).*

When combined with different copper(I) salts ligand **5.3** has been shown to form a variety of architectures ranging from discrete ML_2 and M_6L_2 structures to helical one-dimensional metallopolymers and two-dimensional metallopolymers.[160-165] Ligand **5.3** will also give a helical one-dimensional coordination polymer when reacted with silver(I) perchlorate.[148] The ligand interacts with silver(I) in a manner analogous to the copper(I) at the bottom right of Figure 5.6.

A nitrogen core can accommodate more than two arms, as in triallylamine (**5.4**) which has three allyl arms. Triallylamine has been reacted with copper(I) chloride by Håkansson et al.[166] which resulted in a helical coordination polymer with spontaneous resolution upon crystallisation. Two things of note in this structure are: **5.4** is acting as a bifunctional ligand as both the tertiary nitrogen and an alkene are coordinated to copper(I) and only one of the three alkenes is coordinated.[166]

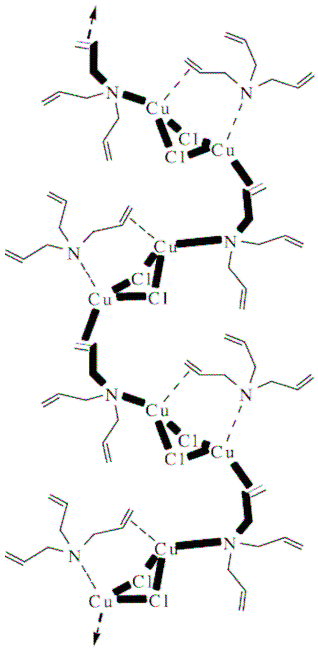


***Figure 5.7** – Schematic of the helical triallylamine copper(I) chloride complex.*[166]

The last ligand of interest is tetra(allyloxy)silane (**5.5**). This ligand is tetradentate and when combined with CuCl it coordinates to four copper units. Each copper unit consists of four copper atoms bridged by four chlorine atoms to form an eight membered ring. A fifth copper atom sits above the middle of the ring and is coordinated to the four chlorine atoms of the ring and a fifth chlorine perpendicular to the plane of the ring. Each such unit has four molecules of **5.5** coordinated which gives a two-dimensional layered framework as seen in Figure 5.8.[110]

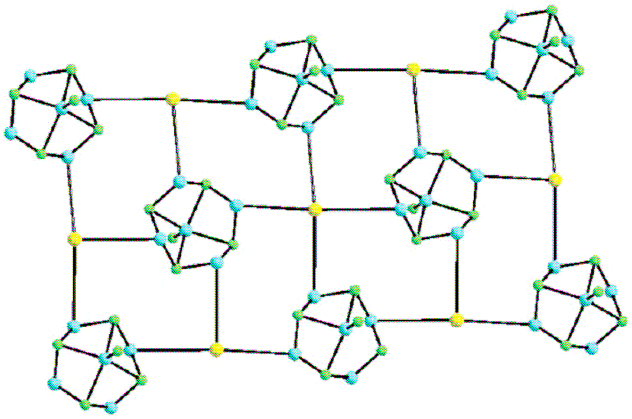


Figure 5.8 *– Schematic of the two-dimensional network made up of* ***5.5*** *and* Cu_5Cl_5 *clusters. The yellow spheres represent ligand* ***5.5****.*[110]

5.2 Ligand Syntheses

Ligands **5.1**, **5.4** and **5.6**, shown in Figure 5.9, cover a range of atom types and geometries at the core of the ligand as well as a varying number of binding domains surrounding the core. Ligand **5.7** incorporates of two carbon cores linked together by oxygen giving rise to a six armed ligand.

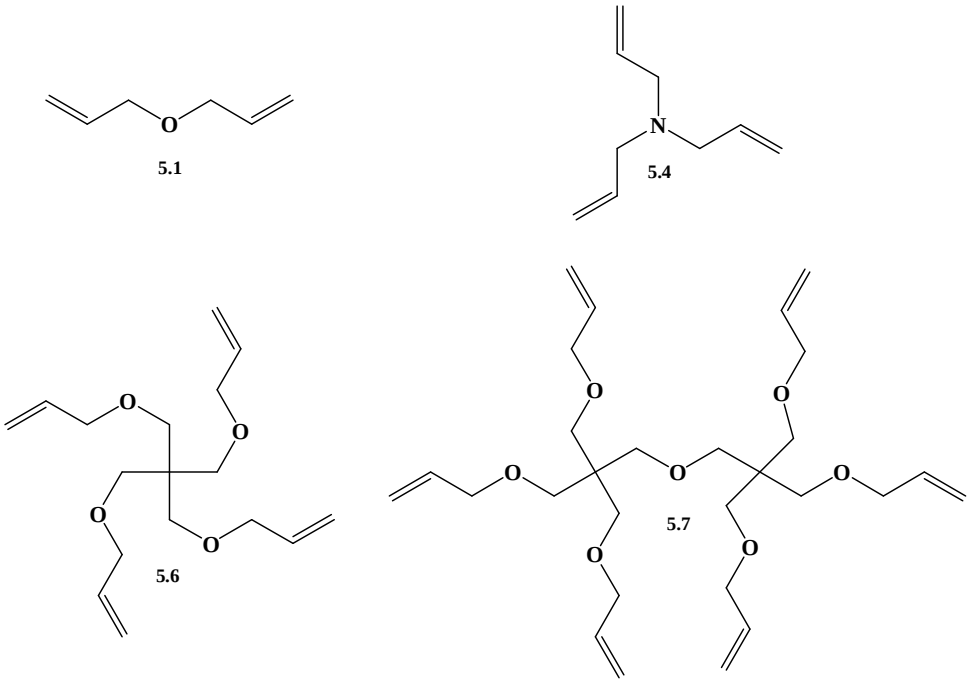
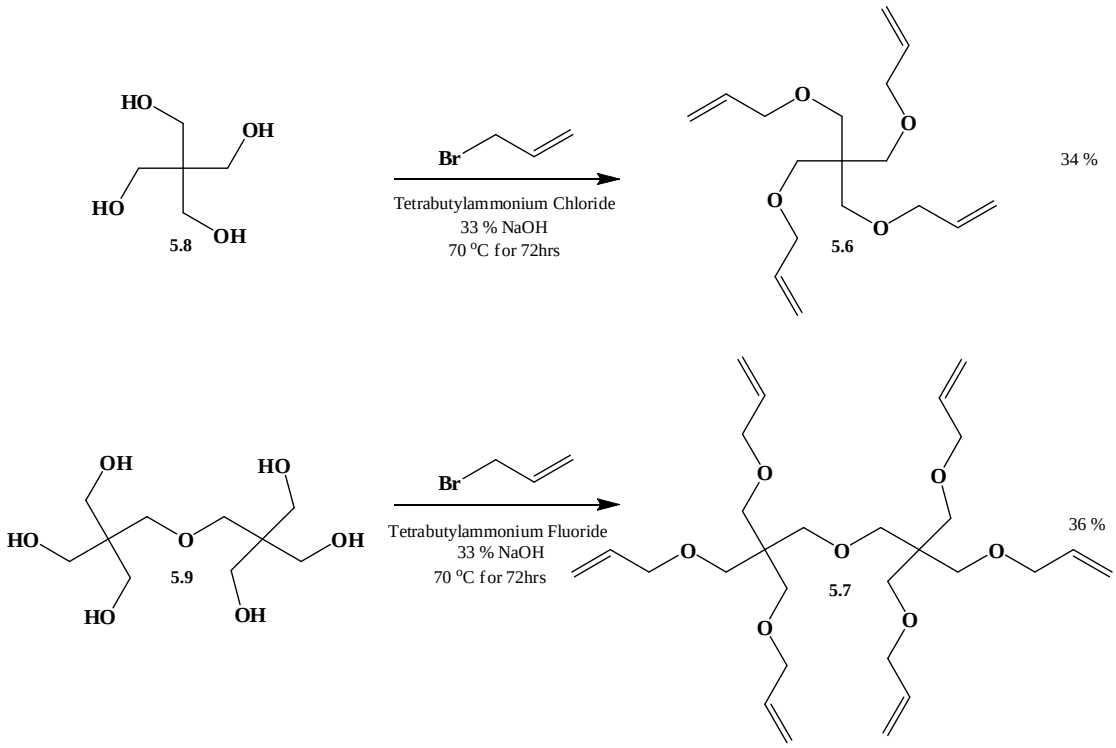


Figure 5.9 *– Ligands used in this chapter.*

Ligands **5.6** and **5.7** are synthesised from the allylation of pentaerythritol (**5.8**) and dipentaerythritol (**5.9**), respectively. As they do not contain phenolic oxygens the acidity of the hydroxyl hydrogens is much less and the mild conditions, used in previous allylation reactions, is not suitable. A literature procedure[167] describing the synthesis of **5.6** was used and then adapted to produce **5.7**. The procedure involves reacting the precursor, **5.8** or **5.9**, with a 5-fold excess of allylbromide in a 33 % sodium hydroxide solution with a small amount of tetrabutylammonium halide. The resulting solution is then heated for three days at 70 °C to give the desired product in modest yields; 34 % for **5.6** and 36 % for **5.7**.



***Scheme 5.1** – Reaction conditions for the synthesis of ligands **5.6** and **5.7**.*

Ligands **5.1** and **5.4** were obtained from commercial sources.

5.3 Complexes of Diallyl Ether

With silver(I) triflate (**5.10**)

The simplest bridging ligand of this series is diallyl ether **5.1**, which has a single oxygen atom at its core and is capable of bridging two silver atoms through two allyl ether arms. When combined with silver(I) triflate it gives a discrete M_2L unit with the incorporation of three water molecules which solved in the orthorhombic space group Pbcm. Through the middle of the unit there is a mirror plane and in the asymmetric unit, which can be seen in Figure 5.10, there is one silver atom, one and a half water molecules, one half of ligand **5.1** and two half triflate counter anions.

As in the analogous copper(I) complexes, ligand **5.1** has both alkenes coordinated and bridges the two metal atoms, as opposed to chelating to a single metal atom. The central oxygen atom within **5.1**, is non-coordinating in this structure, as was also the case in the copper(I) complexes.

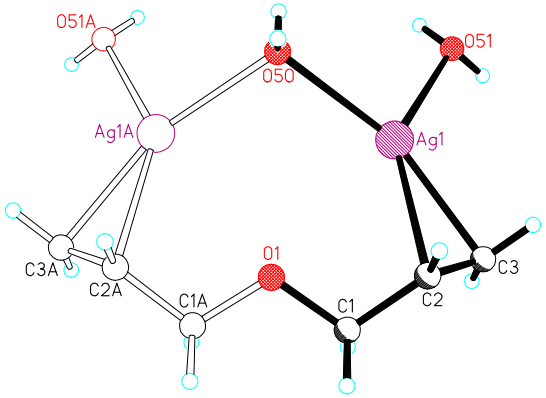


Figure 5.10 *– View of the discrete M_2L unit of* ***5.10****. The triflate counter anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C2 2.363(5), Ag1-C3 2.338(5), Ag1-C2,C3 2.254(5), Ag1-O50 2.374(3), Ag1-O51 2.343(3), O50-Ag1-O51 97.8(2), O50-Ag1-C2,C3 137.2(2), O51-Ag1-C2,C3 124.2(2).*

The two silver atoms within the M_2L unit are bridged by ligand **5.1** and a water molecule. Each silver atom has two water molecules as well as one alkene from ligand **5.1** coordinated and has a distorted trigonal planar geometry. There is only one olefin coordinated to each silver atom and similar to previous example to the C=C centroid to silver distance is shorter at 2.25 Å. The Ag···Ag dstance within the M_2L unit, Ag1 to Ag1A in Figure 5.11, is quite short at 3.79 Å and the Ag···Ag distance between silver atoms in adjacent units, Ag1 to Ag1B, is similar at 3.86 Å. The short distance between M_2L units arises from auxiliary water molecules pseudo-doubly bridging silver atoms from neighbouring units as seen in Figure 5.11.

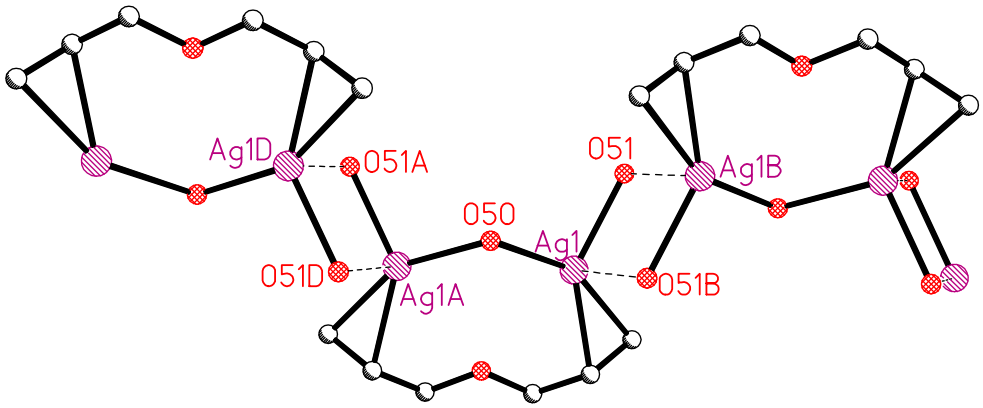


Figure 5.11 *– View of the water molecules pseudo-doubly bridging silver atoms to link M_2L units into a one-dimensional polymer. Hydrogen atoms have been excluded for clarity.*

Of the two bridging water molecules, one is coordinated via the oxygen atom to one silver atom (2.37 Å) and weakly interacts with the other silver atom (2.71 Å) and vice versa for the second water molecule. This links the M_2L units into a one-dimensional polymer.

The triflate counter anions interact with the main structure through a series of hydrogen bonds and weak interactions with silver atoms. One triflate anion, to the right in Figure

5.12, has all of its oxygen atoms involved in hydrogen bonding with the three water molecules within one M_2L unit anchoring it in place.

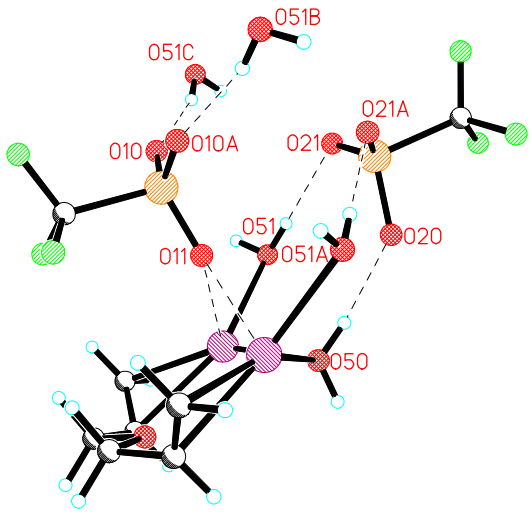


Figure 5.12 *– View of the hydrogen bonding between oxygen atoms on the triflate and water molecules. Fluorine disorder has been omitted for clarity. Selected bond lengths (Å): O50-O20 2.693(3), O51-O21 2.838(3), O10-O51C 2.761(5) Ag1-O11 2.667(5)*

The second triflate anion, to the left in Figure 5.12, has one oxygen atom, O11, weakly interacting with both silver atoms in a bridging manner. The other two oxygen atoms in the second triflate, O10 and O10A, are hydrogen bonded to the hydrogen atoms on O51C and O51B which are from two different M_2L units in a neighbouring strand thus linking the one-dimensional polymers into two-dimensional sheets. The second triflate counter anion is also involved in weak hydrogen bonding between its fluorine atoms and hydrogen atoms on ligand **5.1**. The two-dimensional sheets stack upon each other with no interactions between them.

5.4 Complexes of Triallylamine

With silver(I) perchlorate (**5.11**), hexafluorophosphate (**5.12**), triflate (**5.13**) and nitrate (**5.14**)

Ligand **5.4** was combined with a variety of silver(I) salts, using the same procedure in each instance, which resulted in crystalline complexes with silver(I) perchlorate (**5.11**), hexafluorophosphate (**5.12**), triflate (**5.13**) and nitrate (**5.14**). Complexes **5.12** and **5.13** are isomorphous and crystallise in the orthorhombic space group $Pna2_1$. In contrast, complex **5.11** crystallises in the monoclinic space group $P2_1$ and **5.14** in $P2_1/n$.

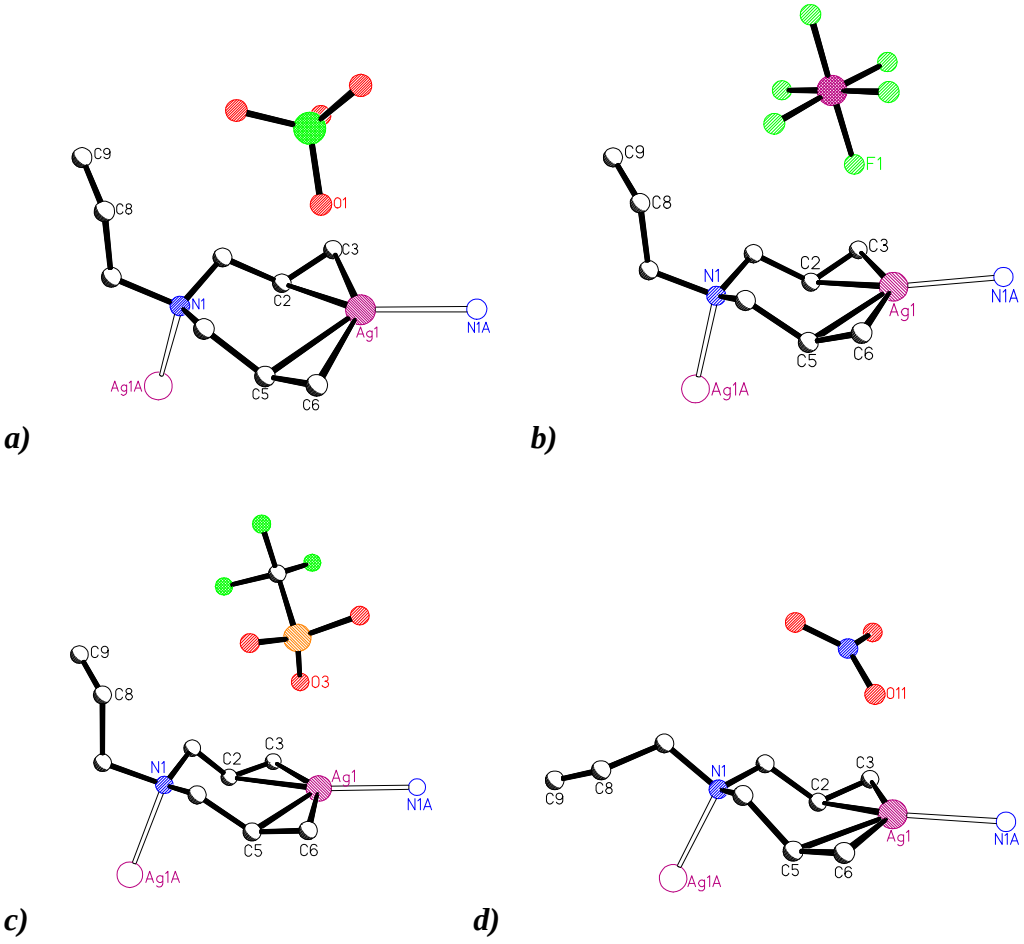


***Figure 5.13** – Comparison of the asymmetric units of **5.11**, **5.12**, **5.13** and **5.14**. Hydrogens have been omitted for clarity. **a)** With silver(I) perchlorate, **5.11** **b)** with silver hexafluorophosphate, **5.12** **c)** with silver(I) triflate, **5.13** **d)** with silver(I) nitrate, **5.14**.*

Each structure has the same asymmetric unit in that it contains one molecule of **5.4**, one silver atom and one non-coordinated counter anion. Ligand **5.4** has been previously shown to act as a bifunctional ligand.[166] In all four silver(I) complexes, both the tertiary nitrogen core and two alkene functional groups coordinate to the silver atoms. The overall connectivity of the resulting structures is the same; ligand **5.4** chelates to a silver atom through two alkenes and bridges to a second silver atom through the tertiary nitrogen giving a one-dimensional metallopolymer. This is very similar to one of the binding motifs seen in diallylamine when combined with copper(I).[165]

	5.11 (Å)	**5.12** (Å)	**5.13** (Å)	**5.14** (Å)
Ag1-N1A	2.296(7)	2.278(4)	2.297(5)	2.300(2)
Ag1-C2	2.422(9)	2.379(4)	2.396(6)	2.416(3)
Ag1-C3	2.346(9)	2.340(4)	2.351(6)	2.372(3)
Ag1-C2,C3	2.288(9)	2.258(4)	2.275(6)	2.299(3)
Ag1-C5	2.407(8)	2.406(4)	2.396(6)	2.404(3)
Ag1-C6	2.355(9)	2.340(4)	2.360(6)	2.354(3)
Ag1-C5,C6	2.283(9)	2.277(4)	2.281(6)	2.282(3)

***Table 5.1** – Selected bond lengths in **5.11**, **5.12**, **5.13** and **5.14**.*

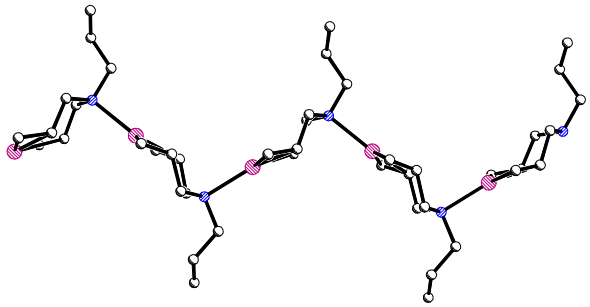
	5.11 (°)	**5.12** (°)	**5.13** (°)	**5.14** (°)
N1A-Ag1-C2,C3	123.0(3)	124.1(1)	122.6(2)	123.0(1)
N1A-Ag1-C5,C6	123.5(3)	122.6(1)	122.6(2)	123.7(1)
C2,C3-Ag1-C5,C6	112.1(3)	112.7(2)	113.0(2)	112.3(1)

***Table 5.2** - Selected bond angles in **5.11**, **5.12**, **5.13** and **5.14**.*

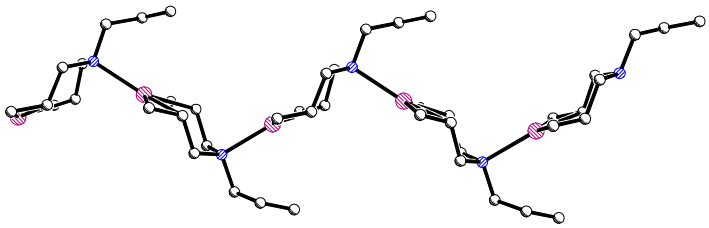
In all examples **5.4** has one non-coordinated allyl arm and this is where, aside from the counter anion, the main difference between the four complexes occur. Complexes **5.11**, **5.12** and **5.13** have the non-coordinated allyl arm pointing up towards the counter anion as shown in Figure 5.13(a,b,c). In complex **5.14**, on the other hand, the non-coordinated allyl arm folds back down away from the counter anion as seen in Figure 5.13(d).

The silver environments are comparable for all four complexes and in all cases the silver atoms are three coordinate with distorted trigonal planar geometry, where the smallest angle is between the two coordinated alkenes. The Ag···Ag distance varies little from

structure to structure with **5.13** the shortest at 4.86 Å, then **5.12** at 4.87 Å followed by **5.11** at 4.92 Å and **5.14** is the longest at 5.02 Å.



a)



b)

Figure 5.14 *– Segments of the one-dimensional polymers comprised of silver(I) and ligand* ***5.4****.* ***a)*** *Section of metallopolymer representing* ***5.11****,* ***5.12*** *and* ***5.13*** ***b)*** *section of metallopolymer representing* ***5.14****.*

The one-dimensional polymers are in a zig-zag conformation with the non-coordinated allyl arm alternatively points up, then down. Figure 5.14(a) shows a representation for complexes **5.11**, **5.12** and **5.13** and Figure 5.14(b) for **5.14**. Weak hydrogen bonding interactions between hydrogen atoms in ligand **5.4** and either oxygen, chlorine or fluorine atoms, depending on the counter anion, hold the metallopolymers together in three-dimensional space.

5.5 Complexes of Tetra-O-allyl-pentaerythritol

With silver(I) perchlorate (**5.15**)

Ligand **5.6** was successfully reacted with silver(I) perchlorate in a chloroform/acetone solvent system. Vapour diffusion of diethyl ether and then evaporation of all solvents, yielded crystals suitable for X-ray analysis. The structure solved in the tetragonal space group I-42d and the asymmetric unit contains one quarter of ligand **5.6**, one half of a silver atom and one half of a disordered coordinating perchlorate anion. The perchlorate anion is disordered over two positions, both of which are coordinating and the dominant position has an occupancy of 55 %.

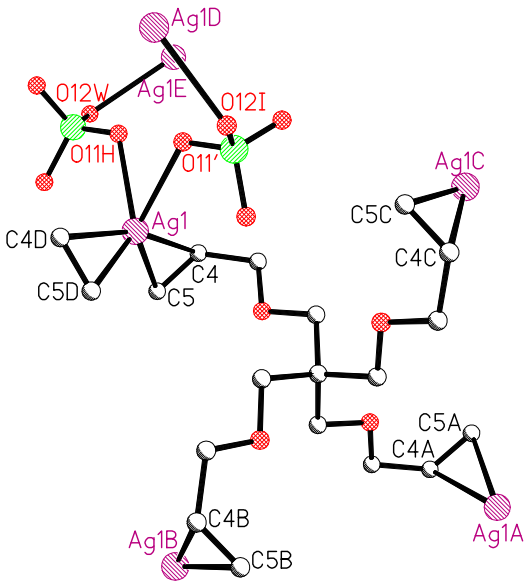
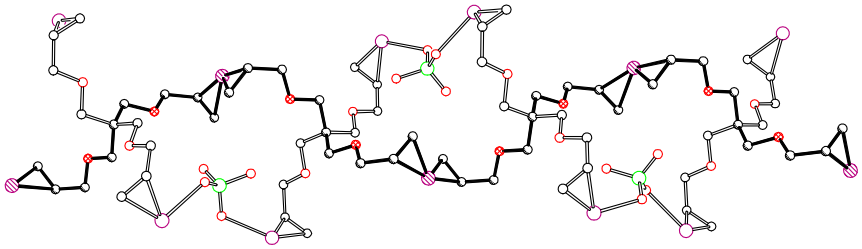


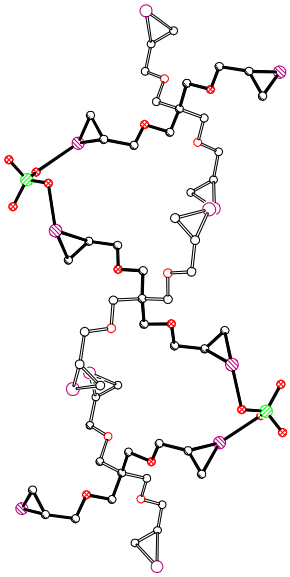
Figure 5.15 *– View of ligand* ***5.6*** *coordinated to four silver atoms in* ***5.15****. Perchlorate disorder and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C4 2.476(3), Ag1-C5 2.356(3), Ag1-C4,C5 2.323(3), Ag1-O11' 2.461(5), Ag1D-O12I 2.499(8).*

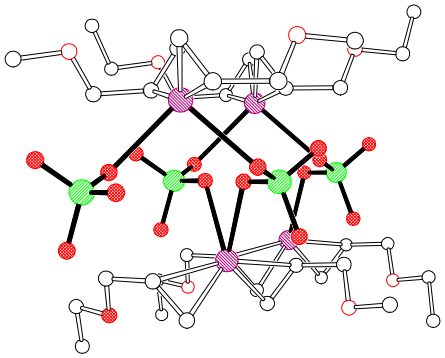
Ligand **5.6**, like the four armed ligands in chapter 4, has all four terminal alkenes coordinated to different silver atoms. Each silver atom is four coordinate with two alkenes and two oxygen atoms, from different perchlorate anions, coordinated. The

geometry about the silver atom ranges from a see-saw conformation to distorted trigonal pyramidal and is dependent on which positions of the disorder are occupied by the coordinated oxygen atoms. The Ag···Ag distance across the ligand, Ag1···Ag1A in Figure 5.15, is 10.38 Å and the distance between the silver atoms around the edge of the ligand, Ag1···Ag1C in Figure 5.15, is 7.55 Å.



a)





b) ***c)***

Figure 5.16 *– Three mode of polymer propagation in* ***5.15****. Disorder and hydrogen atoms have been omitted for clarity.* ***a)*** *Propagating horizontally* ***b)*** *propagating vertically* ***c)*** *propagating into and out of the plane of the page.*

With the higher number of binding domains within ligand **5.6** the resulting architecture of **5.15** has a higher dimensionality, and is more complex than **5.10** and the triallylamine series. Complex **5.15** is a three-dimensional polymer which propagates in two directions through bonding between ligand **5.6** and silver(I). The polymer propagates horizontally, as seen in Figure 5.16(a), through the bridging of silver atoms by two of the allyl ether arms in **5.6** and propagates vertically, as seen in Figure 5.16(b), through the other two allyl ether arms of **5.6**. The perchlorate counter anions alternately bridge silver atoms. These two-dimensional sheets sit directly above and below one another and are linked together into a three-dimensional metallopolymer by silver(I) perchlorate chains as seen in Figure 5.16(c). The silver(I) perchlorate chains are helical in nature, however the complex contains both M and P helices and so does not have overall chirality.

5.6 Complexes of Hexa-O-allyl-dipentaerythritol

Ligand **5.7** was reacted with silver(I) perchlorate, triflate, hexafluorophosphate, borate, nitrate, nitrite and trifluoroacetate. A variety of solvents and solvent mixtures as well as different temperatures, 5 °C and 25 °C, were used. Higher ratios of silver(I) were utilised to promote the coordination of all six alkenes and to encourage the formation of crystalline products. Complexes of **5.7** with silver(I) were not isolated. Ligand **5.7** is very flexible and its numerous allyl ether arms can adopt many possible conformations. This excessive flexibility decreases the ability of any complexes formed to crystallise.

5.7 Summary

This chapter covers a series of four ligands based around single atom ligand cores. Ligands **5.1** and **5.4**, obtained from commercial sources, containing an oxygen and nitrogen core respectively. Ligands **5.6** and **5.7** were synthesised through the allylation of pentaerythritol and dipentaerythritol. Ligand **5.7** is a previously unknown compound.

Ligand **5.1** gave a discrete M_2L unit when reacted with silver(I) triflate with three coordinated water molecules per unit. Ligand **5.4** gave a series of similar one-dimensional polymers when reacted with silver(I) perchlorate **5.11**, hexafluorophosphate

5.12, triflate **5.13** and nitrate **5.14**. In all of the identified complexes **5.4** acted as a tridentate binucleating ligand. Tetradentate ligand **5.6** yielded a complicated three-dimensional polymer when reacted silver(I) perchlorate, where all four binding domains were engaged in coordination to silver atoms. The formation of complexes of **5.7** with silver(I) salts was not successful, probably owing to the extremely flexible nature of the ligand.

Of note within this series is complex **5.10**. It is the first example, within this work, of a silver atom with only one alkene coordinated whereas previously it has either two or three alkenes coordinated. The silver-alkene centroid distance is shorter which is likely due to less crowding around the silver atom.

The work in this chapter demonstrates the ability of the silver(I)-alkene synthon to construct a range of architectures in the absence of aromatic moieties.

Chapter Six

Bi-Functional Ligands

CHAPTER 6

Bi-Functional Ligands

6.1 Introduction

As seen in the previous chapters, ligands can be varied in many ways including: changing the core, adding spacer groups and having two, three, four or six binding domains. The last ligand variation to be covered in this work is to alter the functional groups. Ligands that contain an alkene as well as either an oxygen atom or heterocyclic nitrogen atom will be deliberately used to induce silver(I) to bind to more than one type of functional group within the same complex. The ultimate goal of using these ligands is to bridge silver atoms to create new architectures.

There are previous literature reports of silver(I) atoms that have both heterocyclic nitrogen atoms and an olefin coordinated. In many of these cases, the two functional groups are not within the same ligand.[62-66] There are some examples of silver(I) complexes that are comprised of silver(I)-arene and silver(I)-nitrogen interactions and these use mostly fulvene based ligands[168,169] as shown in Figure 6.1. There is an additional example which uses a tripodand ligand[170] also shown in Figure 6.1.

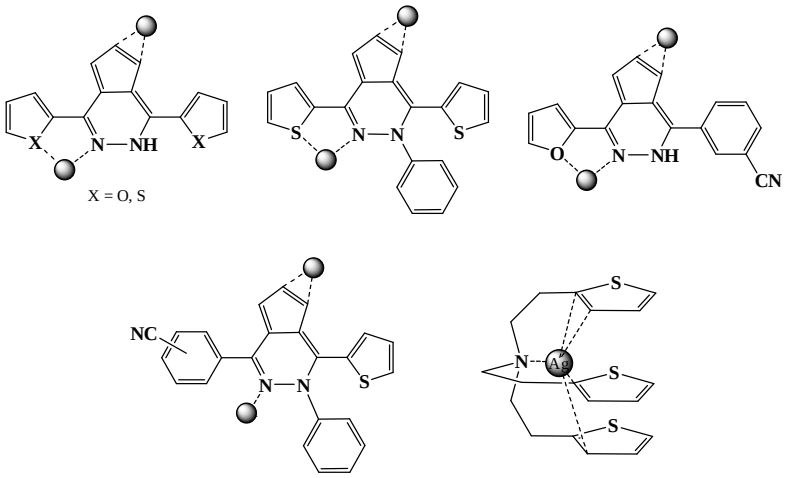
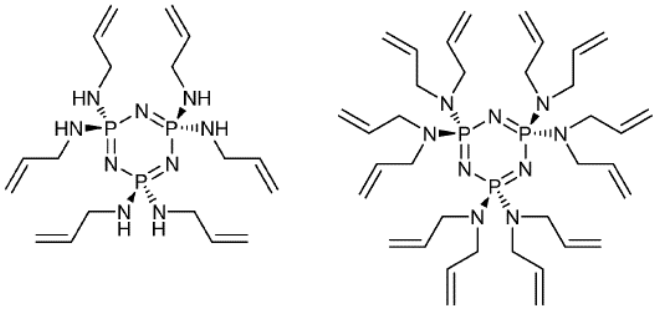


Figure 6.1 *– Silver(I) coordinating to both a heterocyclic nitrogen atoms and an arene within the same ligand.*

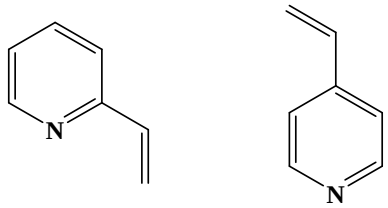
A recent example of ligands that will coordinate to silver through both an olefin and a nitrogen are two allylated phosphazenes; hexakis-(allylamino)-cyclotriphosphazene (**HAACTP**) and hexakis-(diallylamino)-cyclotriposphazene (**HDAACTP**).[171]



HAACTP **HDAACTP**

Figure 6.2 *– Allylated cyclotriphosphazene ligands.*

HAACTP forms a one-dimensional polymer with all nine potential donors coordinated to three different silver atoms. Over a period of weeks some of the one-dimensional polymer decomposes and the rest converts into an isomeric three-dimensional polymer. **HDAACTP** on the other hand forms a (**HDAACTP**)Ag_5 unit with all fifteen binding sites in use coordinating to five silver atoms. These units are linked together into a network by counter anions and methanol molecules.[171]



6.1 **6.2**

Figure 6.3 *– Simple molecules that contain a heterocyclic nitrogen and an alkene.*

An initial inspiration for this thesis was a complex that contained ligand **1.21** as it coordinated to silver(I) through both an olefin and heterocyclic nitrogens.[93] From this, initial studies were carried out within the department that investigated vinylpyridines as potential ligands, as these are the simplest molecules that contain both a pyridine ring and an alkene. Two commercially available isomers were used, 2- (**6.1**) and 4-vinylpyridine (**6.2**), and were reacted with a variety of silver(I) salts in a 1:1 ratio.

Initially complexes, shown in Figure 6.4(a,b), were obtained of both **6.1** and **6.2** with silver(I) perchlorate revealing simple discrete structures that have a central linear silver atom with the two ligands coordinated through only the nitrogen atoms. A third complex, Figure 6.4(c), was isolated from the reaction of **6.2** with silver nitrate which proved to be similar in nature to the perchlorate complex.

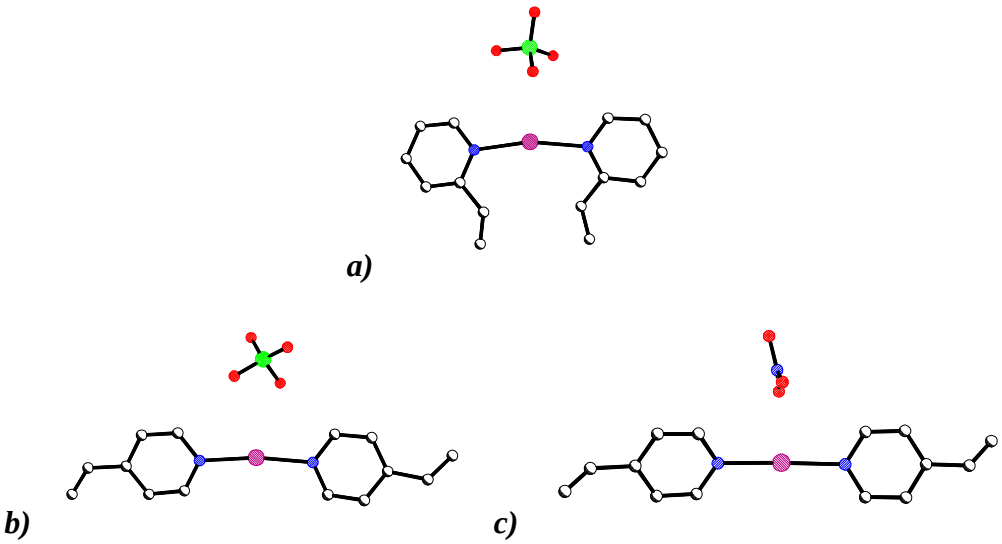


Figure 6.4 *– Simple ML_2 structures formed with vinylpyridine and silver(I) when mixed in a 1:1 ratio. Hydrogen atoms have been omitted.* ***a)*** *Showing ligand* ***6.1*** *with silver(I) perchlorate* ***b)*** *showing ligand* ***6.2*** *with silver(I) perchlorate* ***c)*** *showing ligand* ***6.2*** *with silver(I) nitrate.*

Silver(I) perchlorate was then taken and reacted again with ligands **6.1** and **6.2** but this time in a ten-fold excess. The same complex was formed with ligand **6.1**; however a new complex with ligand **6.2** was isolated. The new complex was a one-dimensional polymer,

shown in Figure 6.5, which demonstrates the ability of ligand **6.2** to bridge silvers by utilising both the heterocyclic nitrogen and the alkene.

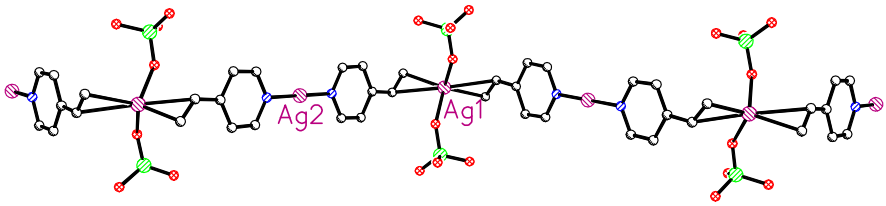
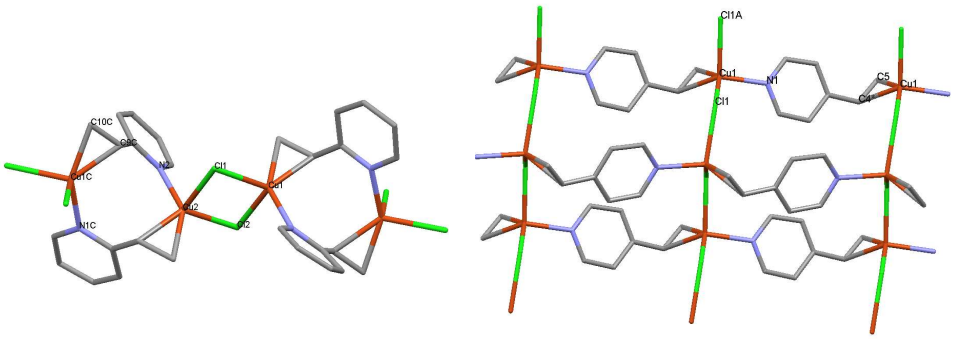


***Figure 6.5** – One-dimensional polymer that forms when ligand **6.2** is reacted with an excess of silver(I) perchlorate. Hydrogen atoms have been omitted.*

As mentioned in the previous chapter, there are many literature examples of complexes that utilise the copper(I)-alkene interaction to construct metallosupramolecular assemblies. The concept of reacting ligands that include both heterocyclic nitrogen atoms and olefinic groups with copper(I) has also been explored in the literature using ligands **6.1** and **6.2**. A systematic study of the products from a 1:1 reaction between CuCl, CuBr and CuI and **6.1** and **6.2** was carried out by Engelhardt et al.[172] in the late 1980s. It was found that CuI gives a very similar one-dimensional polymer with both **6.1** and **6.2**. The polymeric nature of the complex arose from a 'stair-shaped' CuI backbone to which the ligands were coordinated through the heterocyclic nitrogen. There were no copper(I)-alkene interactions.

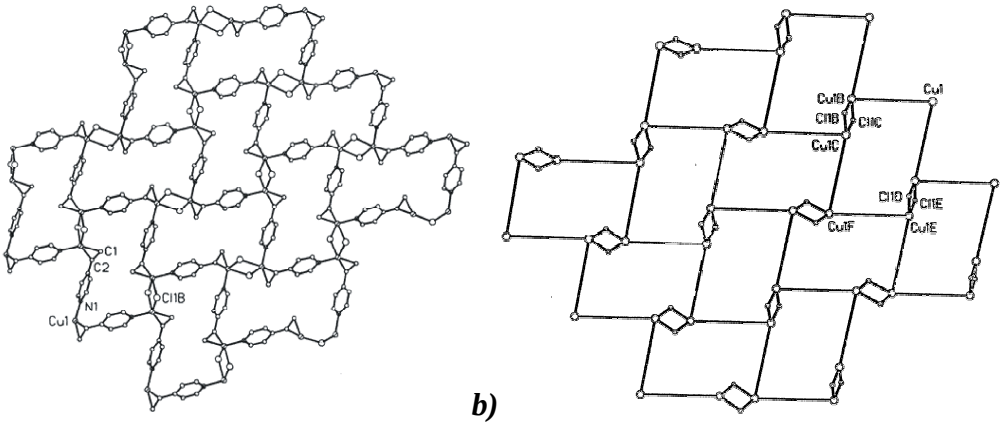
The results from the reactions of **6.1** and **6.2** with either CuBr or CuCl were more interesting as all four complexes displayed copper(I)-alkene interactions. Ligand **6.1** gave very similar one-dimensional metallopolymers with both CuBr and CuCl. Each polymer consisted of Cu_2X_2 units, X=Cl, Br, being doubly bridged by ligand **6.1** where the ligand was coordinated to one copper by the nitrogen and coordinated to the second copper by the alkene as seen in Figure 6.6(a)



a) ***b)***

Figure 6.6 *– Complexes of* ***6.1*** *and* ***6.2*** *with CuCl* ***a)*** *View of ligand* ***6.1*** *bridging Cu_2Cl_2 units* ***b)*** *view of ligand* ***6.2*** *bridging $(CuCl)_n$ strands.*

Ligand **6.2** gave isomorphous two-dimensional metallopolymers when reacted with either CuBr or CuCl. These complexes differ from the copper(I) complexes with ligand **6.1** in that **6.2** is now bridging one-dimensional strands of copper halide, $-(CuX)_n-$ (X = Cl, Br) as opposed to Cu_2X_2 units. A second polymorph of **6.2** with CuCl was identified by Zhang et al.[142] in 2002. The new polymorph was formed under hydrothermal conditions from a 1:2 metal to ligand ratio. In this complex **6.2**, similar to **6.1**, is now bridging Cu_2Cl_2 fragments which has a significant affect on the topology of the two-dimensional metallopolymer as seen in Figure 6.7.



a) ***b)***

Figure 6.7 *– Polymorph of* ***6.2*** *with CuCl* ***a)*** *View of the rectangular grid* ***b)*** *simplified view of the brick-wall type two-dimensional framework in which long straight lines and open circles of increasing size represents* ***6.2****, Cl^- and Cu^+ respectively.*[142]

Other ligands, shown in Figure 6.8, have been found to bridge copper(I) through both Cu(I)-N and Cu(I)-olefin interactions including **6.3**,[110,173] **6.4**,[142,173] **6.5**,[142] **6.6**,[110] **6.7**[174] and **6.8**.[175] Ligands **6.3**[173] and **6.4**[173] have also been shown to have additional Cu(I)-O interactions between copper(I) and the deprotonated carboxy acid group within the ligand.

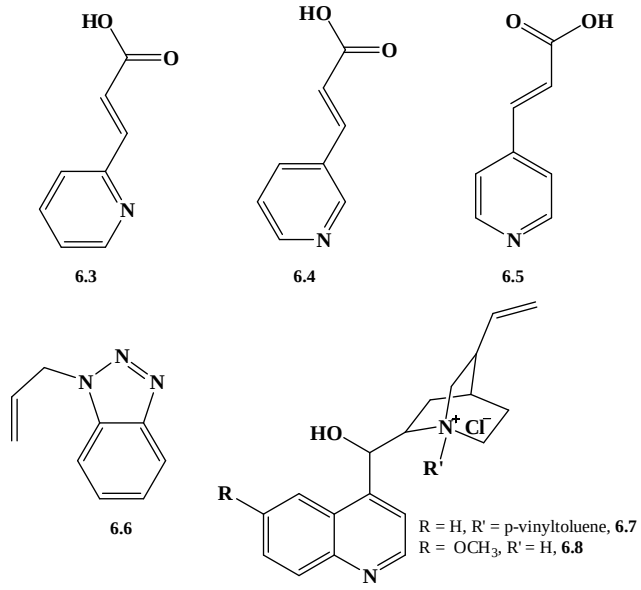


Figure 6.8 *– Ligands shown to interact with copper(I) through both the olefin moiety and the heterocyclic nitrogen.*

An exploitable feature of ligands that contain different functional groups is that they can be designed to possess different binding domains that will favour some metals over others. This allows the controllable formation of mixed metal assemblies which have vast potential applications in material science such as reversible gas storage, catalysis, photoluminescence and semi-conducting properties.[176]

There are two general approaches that can be taken in creating a mixed metal assembly. The first is to incorporate all the required components in a single pot reaction. An example of this is the formation of a mixed metal three-dimensional open framework when Cu(II) and Zn(II) acetate is combined with isonicotinate as the ligand in water with boronic and hydrochloric acid under hydrothermal conditions.[177] Isonicotinate

coordinates to copper(II) and zinc(II) through both the heterocyclic nitrogen and the deprotonated carboxy oxygen as seen in Figure 6.9.

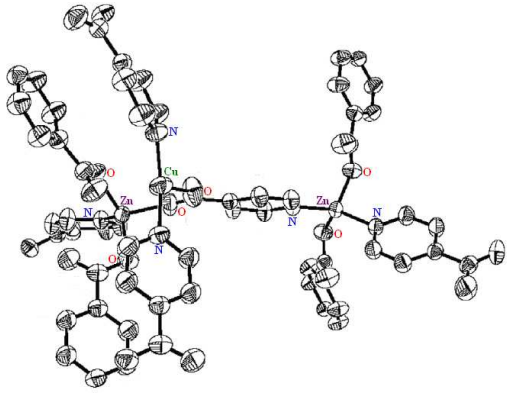


Figure 6.9 *– Basic building unit of the copper(II) and zinc(II) three-dimensional open framework. Hydrogen atoms have been omitted.* [177]

The second approach is the step-wisely construction of a metal-centred ligand and then combine it with the second metal. A good example of this approach is demonstrated in a paper by Chen et al.[178] with the formation of two different metal-organic frameworks both of which are shown in Figure 6.10. A copper(II) complex, bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II) (**6.9**), was initially made as an extended 4,4'-bipyridine analogue which contains Lewis-base nitrogen atoms and Lewis-acid copper sites. The metal-centred ligand **6.9** is then combined, through simple solvent layering, with either $CdCl_2$ or $Cd(NO_3)_2$ to give a one-dimensional ladder and a two-dimensional square grid, respectively.[178]

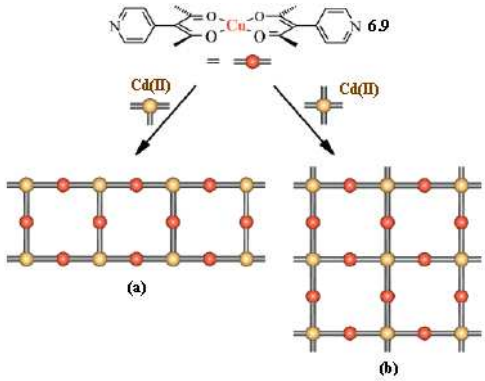


Figure 6.10 *– Schematic of the products formed by the reaction of metal-centred ligand* ***6.9*** *with (a) $CdCl_2$ and (b) $Cd(NO_3)_2$.*[178]

The work within this chapter expands on the work described above; namely silver(I) with ligands **6.1** and **6.2**. A series of three allyloxypyridine isomers; 2- (**6.10**), 3- (**6.11**) and 4- (**6.12**) substituted, has been synthesised. In these isomers the alkene moiety has a much greater degree of freedom than it does in **6.1** and **6.2**. In addition 2,6-di(allyloxy)pyridine (**6.13**) has been synthesised as this allows the use of higher denticities in these bi-functional ligands. The ligands have been reacted with a variety of silver(I) salts in a 1:5 ligand to silver ratio. In addition they have been reacted with the copper(I) halides, CuI, CuCl and CuBr.

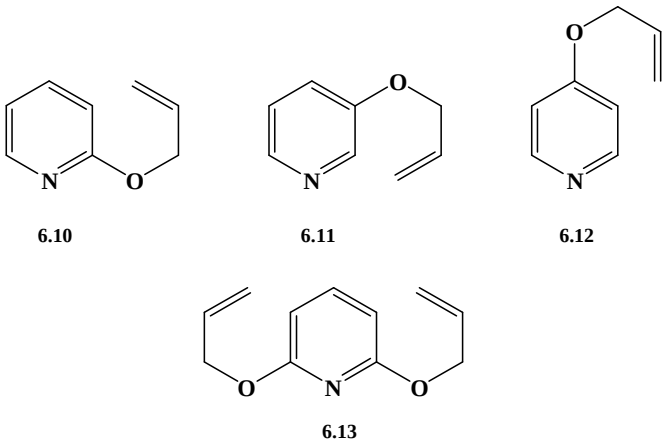
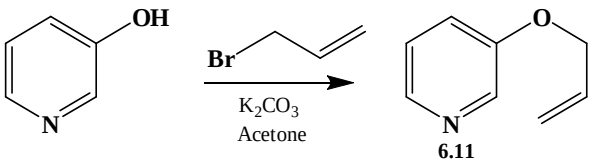


***Figure 6.11** – Selected bi-functional ligands.*

Attempts have also been made to synthesise mixed metal compounds using ligand **6.2** and silver(I) along with additional transition metals as the basic building blocks.

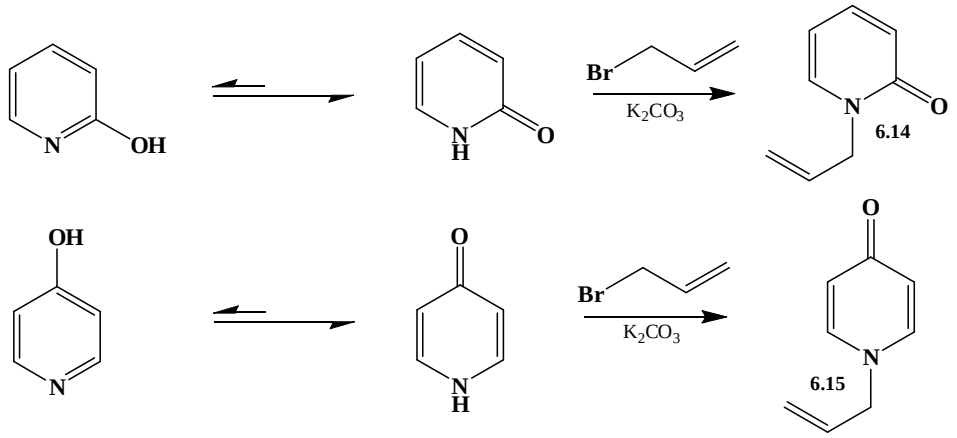
6.2 Ligand Synthesis

The synthetic procedure for the addition of allyl ether substituents, which has been used extensively throughout this thesis, was suitable for the preparation of ligand **6.11** as shown in Scheme 6.1.



***Scheme 6.1** – Synthesis of ligand **6.11**.*

However this methodology is not applicable to the synthesis of ligands **6.10** and **6.12** as the precursors are in equilibrium with their tautomers and the reaction yields the N-allylated product.

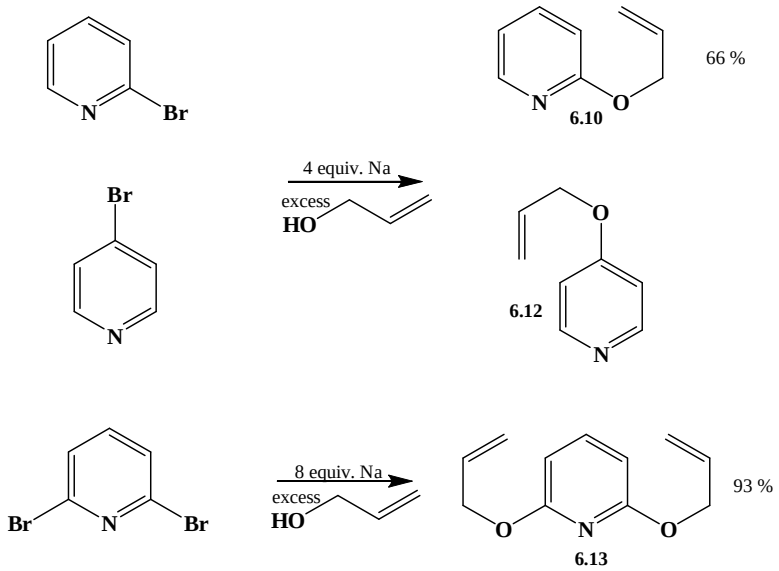


***Scheme 6.2** – Tautomeism of 2- (**6.14**) and 4- (**6.15**) hydroxypyridine to give the N-allylated product.*

However the formation of the N-allylated product in not undesirable as it allows the creation of two new ligands, **6.14** and **6.15,** as shown in Scheme 6.2. These two ligands give the opportunity to expand on the range of bi-functional ligands by having a carbonyl oxygen and an alkene within the same ligand. **6.15** was not synthesised during this work due to the un-availability of the 4-hydroxylpyridine precursor.

An alternative approach to the attachment of allyl ether substituents to pyridine is to use an allyl alcohol in combination with a bromopyridyl precursor. This synthetic procedure for the formation of **6.10** is detailed in the literature by Westwell and Williams[179] and was used for the synthesis of **6.10**, **6.12** and **6.13**.

The new procedure, shown in Scheme 6.3, involves taking four equivalents (eight for the dibromopyridine) of sodium metal and adding it to an excess of allyl alcohol and allowing the mixture to react for one hour. One equivalent of the appropriate bromopyridine precursor is then added and the reaction mixture is heated for twenty hours. The mixture is then cooled by the addition of water and the product is extracted with diethyl ether. Ligand **6.13** has not been reported previously.



Scheme 6.3 *– Reaction scheme for the synthesis of ligands* ***6.10****,* ***6.12*** *and* ***6.13****.*

Previous work has shown the effect of the silver(I) to ligand ratios on the nature of the products. In this chapter, silver complexes with ligands **6.10**, **6.11**, and **6.12** were prepared using a five-fold excess of silver(I). Ligands **6.13** and **6.14** were reacted with silver(I) in a two and a half and two-fold excess, respectively.

6.3 Complexes of 2-Allyloxypyridine

With silver(I) perchlorate (**6.16**)

A solution of **6.10** in chloroform was added to a five-fold excess of silver(I) perchlorate in acetone and within minutes crystals suitable for X-ray analysis had precipitated. The structure solved in the monoclinic space group C2/c. The asymmetric unit of **6.16**, shown in Figure 6.12, contains one silver atom, one molecule of **6.10** and two non-coordinating half perchlorate anions, with one half perchlorate disordered. The overall structure is a discrete M_2L_2 'clip'-type unit.

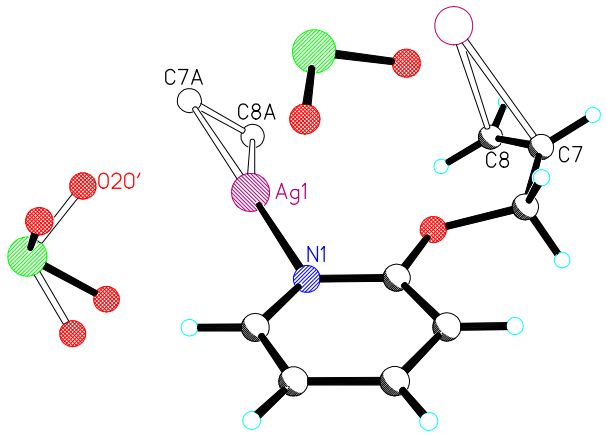
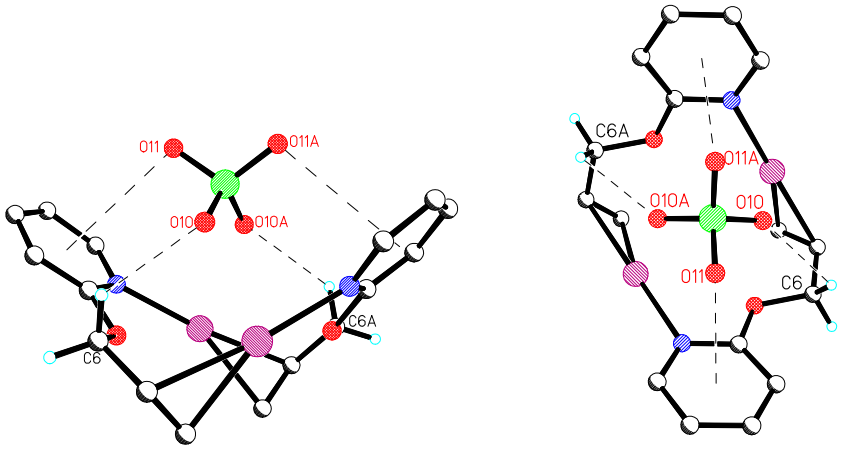


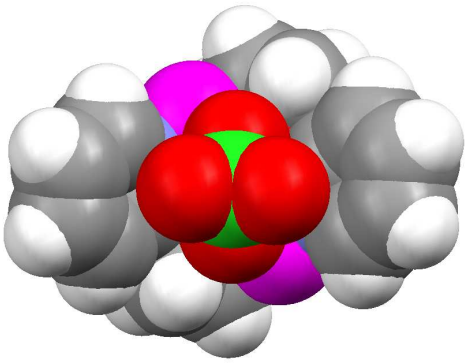
Figure 6.12 *– View of the asymmetric unit of* ***6.16****. Selected bond lengths (Å) and angles (°): Ag1-N1 2.189(2), Ag1-C7A 2.374(2), Ag1-C8A 2.322(2), Ag1-C7A,C8A 2.251(2), Ag1···O20' 2.683(1), N1-Ag1-C7A,C8A 169.2(2).*

The silver atom in **6.16** is two coordinate with a pyridine nitrogen and an alkene bound. It has a distorted linear geometry with an angle of 169.2(2) °. The distortion from linearity is due to a weak interaction between O20' from one of the counter anions and the silver. Each silver atom within a discrete M_2L_2 unit is doubly bridged by ligand **6.10**, which bridges through the pyridine nitrogen and the alkene. The Ag···Ag separation within the discrete units is 4.12 Å and is 6.82 Å between silver atoms in adjacent units.

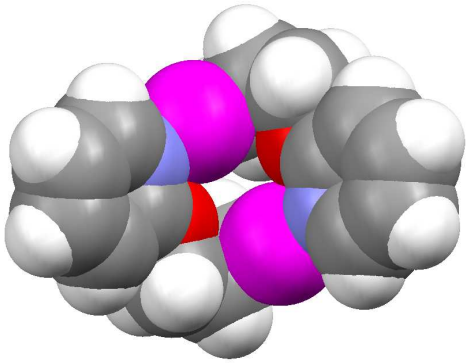
In **6.16**, ligand **6.10** is coordinated to two silver atoms and bridges them through both the nitrogen and the olefinic functional groups. The carbon atoms of the double bond are closer to the silver atom which has also been seen in previous chapters where there is only one coordinated alkene. The distance between the C7A,C8A centroid and Ag1 in **6.16** is 2.25 Å. The planes of the pyridine rings of the two ligands within a discrete unit are at right angles (89.6 °).



a) ***b)***



c)



d)

Figure 6.13 *– M_2L_2 unit clipping a perchlorate counter anion. Relevant hydrogen atoms have been included.* ***a)*** *Side view of clip* ***b)*** *birds eye view of clip* ***c)*** *space filling diagram showing perchlorate sitting in the clip's cavity* ***d)*** *space filling diagram showing the empty cavity.*

As alluded to previously, an interesting feature of this structure is the way in which the M_2L_2 unit effectively 'clips' one of the perchlorate counter anions. The perchlorate anion sits in the cavity made by the clip and is held in position by anion-π interactions (3.33 Å) and a series of weak hydrogen bonds (2.46 – 2.70 Å) as seen in Figure 6.13.

The discrete units of **6.16** pack together within the crystal structure with offset π-π stacking (3.28 Å) between pyridine rings and numerous weak hydrogen bonding interactions between oxygen atoms on both perchlorate anions and hydrogen atoms on ligand **6.10**.

With silver(I) triflate (**6.17**)

Ligand **6.10**, in chloroform, was mixed with a five-fold excess of silver(I) triflate dissolved in acetone. The resulting solution underwent diethyl ether diffusion and was then allowed to slowly evaporate. This process yielded a crystalline compound **6.17**. The crystalline material was suitable for single crystal X-ray analysis and the structure solved in the triclinic space group P-1. The asymmetric unit contains one silver atom, one organic ligand **6.10** and one coordinated triflate counter anion.

As in the previous complex, **6.16**, each silver atom has a pyridine nitrogen and an alkene coordinated but in this complex the counter anion is coordinating and each silver atom has two additional oxygen atoms from different counter anions coordinated, as seen in Figure 6.14. The calculated τ_4 value is 0.82 indicating a distorted trigonal pyramidal geometry. The resulting structure is similar to **6.16** in that two molecules of **6.10** doubly bridge two silver atoms. However in **6.17** what would have been discrete M_2L_2 units are now joined together by the doubly bridging triflate counter anions forming a one-dimensional polymer. An analogous one-dimensional polymer morphology is seen in complex **3.22** in chapter three. However it arises from a ligand containing only alkene functional groups.

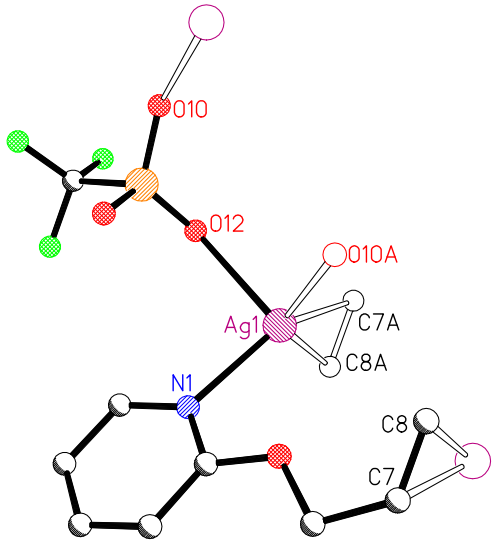
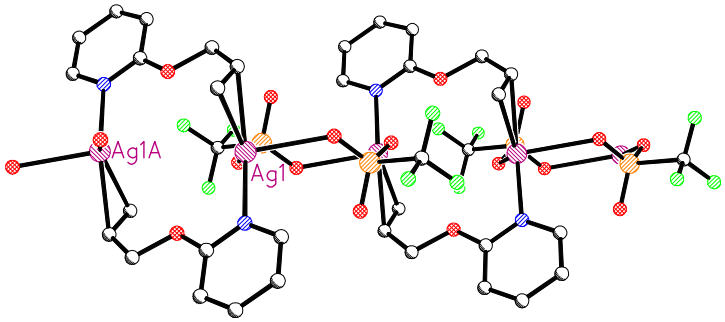


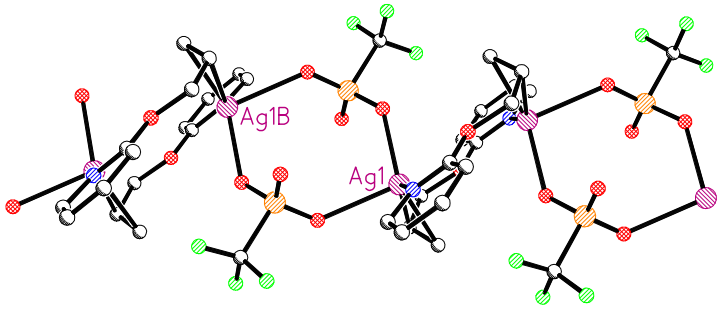
Figure 6.14 *– View of the asymmetric unit of* ***6.17****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.258(9), Ag1-O10 2.331(9), Ag1-O12 2.541(9), Ag1-C7A 2.44(1), Ag1-C8A 2.38(2), Ag1-C7A,C8A 2.32(2), N1-Ag1-O10 111.4(3), N1-Ag1-O12 97.2(4), N1-Ag1-C7A,C8A 126.02(5), O10-Ag1-C7A,C8A 119.05(4), O12-Ag1-C7A,C8A 91.32(4), O10-Ag1-O12 100.9(3).*

Ligand **6.10** is coordinated to the two silver atoms in much the same manner as in **6.16**, where the ligand bridges two silver atoms through coordination of the nitrogen and the olefinic functional group.

The Ag···Ag separation between silver atoms doublybridged by ligand **6.10**, Ag1A···Ag1 in Figure 6.15(a), is marginally longer than in **6.16** at 4.25 Å. The distance between silver atoms doubly bridged by two triflate anions, Ag1···Ag1B seen in Figure 6.15(b), is 5.55 Å which is comparable to the distance between silver atoms doubly bridged by triflate counter anions in **3.22**. As can be seen in Figure 6.15 the complex no longer 'clips' the counter anion as in **6.16** and the planes of the pyridine rings in the repeating M_2L_2 unit are now parallel to each other as opposed to being at right angles in **6.16**.



a)



b)

Figure 6.15 *– View of a section of the polymer* ***6.17****. Hydrogens have been omitted for clarity.* ***a)*** *View of ligand* ***6.10*** *doubly bridging silver atoms* ***b)*** *view of the triflate counter anions doubly bridging silver atoms.*

The one-dimensional polymers pack together with offset π-π stacking between pyridine rings of different strands (3.48 Å) as well as weak hydrogen bonding occurring between the non-coordinating oxygen on the triflate anion and a methylene hydrogen and an arene hydrogen from neighbouring strands (2.44 - 2.53 Å).

6.4 Complexes of 3-Allyloxypyridine

With silver(I) perchlorate (**6.18**)

Ligand **6.11** was combined with a five-fold excess of silver perchlorate in the same procedure as detailed for **6.16** in which colourless crystals suitable for X-ray analysis formed rapidly from the solution. The structure solved in the monoclinic space group

C2/c. The asymmetric unit, seen in Figure 6.16, contains one molecule of ligand **6.11**, one silver atom and a coordinated perchlorate counter anion.

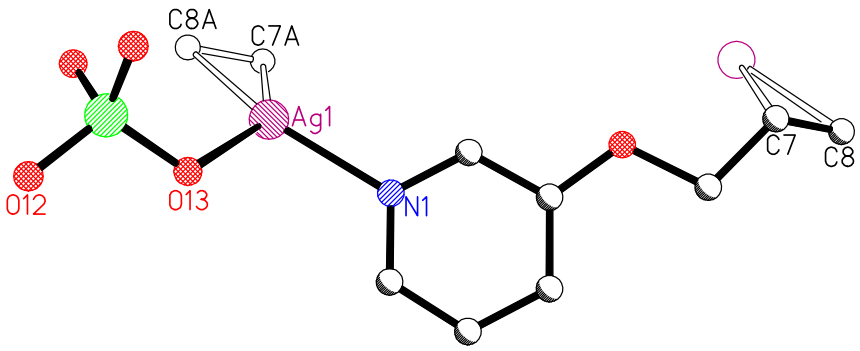


Figure 6.16 *– The asymmetric unit of* ***6.18****. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.228(3), Ag1-O13 2.433(3), Ag1-C7A 2.355(4), Ag1-C8A 2.340(4), Ag1-C7A,C8A 2.251(4), N1-Ag1-O13 89.9(1), N1-Ag1-C7A,C8A 136.3(1), O13-Ag1-C7A,C8A 133.0(1).*

Silver atoms in **6.18** are three coordinate with distorted trigonal planar geometry. Each silver atom has one pyridine nitrogen, one alkene and one perchlorate oxygen coordinated. The distance between the alkene centroid and the silver atom is again of a shorter length, 2.25 Å, which is characteristic for silver atoms with only one alkene coordinated. Additionally there is a weak long range interaction between O12 from a second perchlorate anion and the silver atom (2.71 Å).

Ligand **6.18** is coordinated to two silver atoms and bridges them by coordinating to one silver through the pyridine nitrogen and then to the second silver through the alkene functional group. This is the same double bridging motif as ligand **6.10** seen in both complexes **6.16** and **6.17** with **6.11** forming similar M_2L_2 units. With the change of the substitution pattern from *ortho* in ligand **6.10** to *meta* in ligand **6.11** the Ag···Ag distance between two silver atoms is increased. It changes from 4.12 – 4.25 Å in **6.16** and **6.17** to 7.68 Å in **6.18**, Ag1A···Ag1G (Figure 6.17). Silver atoms from adjacent units, Ag1A and Ag1E, are held closely together at a distance of 4.86 Å as two perchlorate anions

alternatively coordinate to one silver with one oxygen and weakly interact with a second oxygen to the second silver atom (2.71 Å) in a double bridging type manner shown in Figure 6.17. This type of pseudo-double bridging of silver by two perchlorate anions was also seen in complex **2.10**.

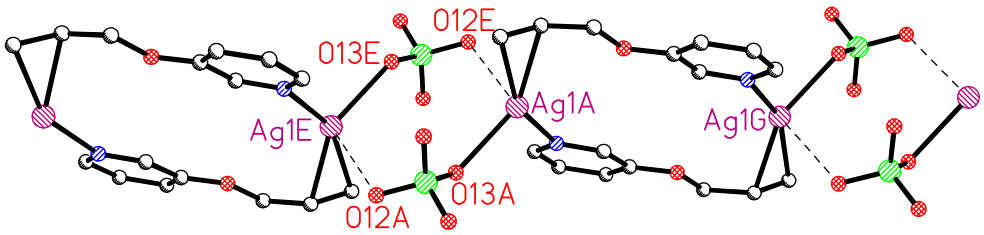


Figure 6.17 *– View of the perchlorate anion pseudo-doubly bridging silver atoms in* ***6.18****.*

The one-dimensional chains of weakly held M_2L_2 units interact with each other through a network of weak hydrogen bonds between the oxygen atoms on the perchlorate and various hydrogen atoms in ligand **6.11** (2.48 - 2.65 Å).

With copper(I) iodide (**6.19**)

As part of attempts to use a different d^{10} metal, ligand **6.11** was reacted with copper(I) iodide in a 1:1 ratio in methanol with constant stirring for 72hrs. Upon cessation of stirring slow evaporation of the solvent yielded crystals of complex **6.19** suitable for single crystal X-ray diffraction. The structure solved in the monoclinic space group $P2_1/c$ and disappointingly revealed that in this complex, ligand **6.11** does not coordinate to copper through the alkene in the allyl ether arm. The allyl ether arm is disordered over two positions with 67 % occupancy in the position shown with in bold in Figure 6.18. Ligand **6.11** is coordinated to copper, but only through the pyridine nitrogen and is not bridging. The Cu-N bond length is normal.[172]

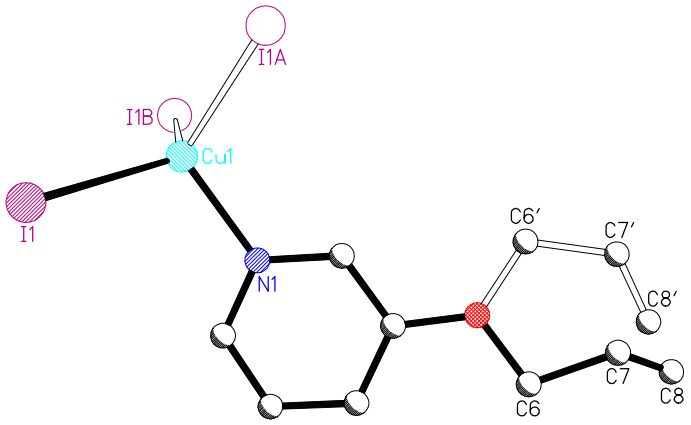
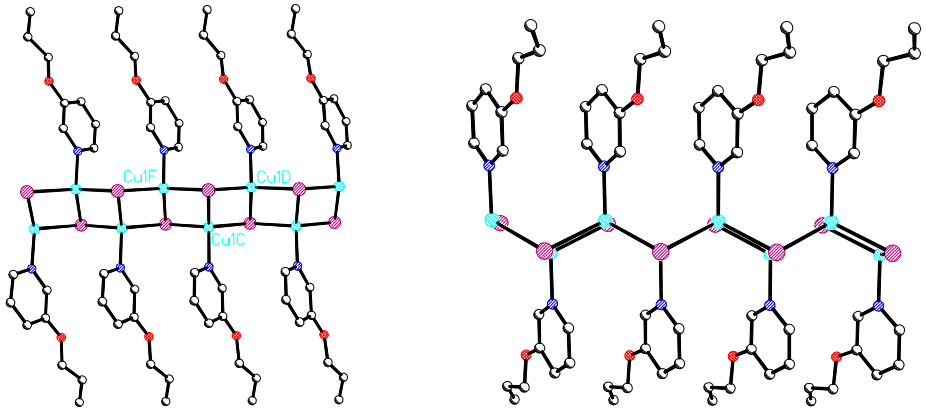


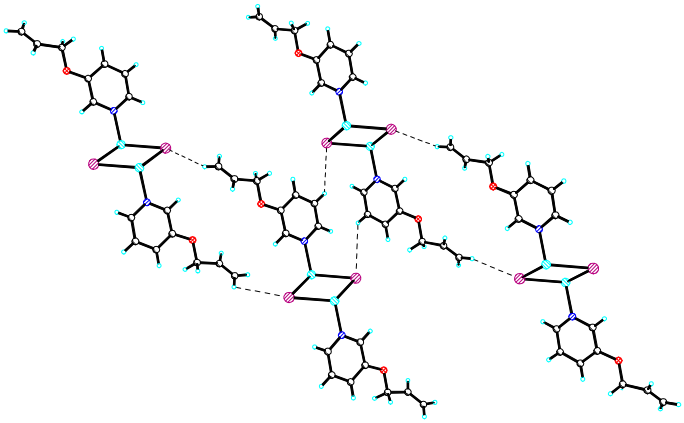
Figure 6.18 *– Asymmetric unit of* ***6.19*** *with disorder in the allyl ether arm. Selected bond lengths (Å) and angles (°): Cu1-N1 2.050(5), Cu1-I1 2.6563(8), Cu1-I1A 2.6445(6), Cu1-I1B 2.6685(6), N1-Cu-I1 106.3(1), N1-Cu1-I1A 108.3(1), N1-Cu1-I1B 106.68(9), I1-Cu1-I1A 116.16(2), I1A-I1-Cu1-I1B 114.41(2), Cu1-I1B 104.53(3).*

The copper in **6.19** is four coordinate with a calculated τ_4 value of 0.92 indicating the geometry is between trigonal pyramidal and tetrahedral. Each copper has three iodide anions coordinated as well as one molecule of **6.11**. CuI has dimerised into Cu_2I_2 squares and the overall structure is a one-dimensional ladder propagated through an infinite chain of fused Cu_2I_2 squares. Ligand **6.11** is essentially coordinated to a one-dimensional copper iodide backbone seen in Figure 6.19(a). The structure and connectivity of **6.19** is very similar to the complexes of CuI with ligands **6.1** and **6.2**.[172]

Within the polymer the pyridine ring interacts with neighbouring rings through offset π-π stacking (3.46 Å) as shown in Figure 6.19(b). One-dimensional chains pack together to accommodate the weak C-H···I interactions between aromatic or olefinic hydrogen atoms and iodide in the copper iodide backbone (3.17 and 3.20 Å) as shown in Figure 6.19(c). The C-H···I interactions of the olefinic hydrogen atoms only occur when the allyl ether is in the dominate occupancy.



a) ***b)***



c)

Figure 6.19 *– **a)** View of the one-dimensional polymeric nature of **6.19** **b)** view of the zig-zagged nature of the copper iodide backbone and π-π stacking between pyridine rings **c)** displaying the weak C-H-I interactions between polymer strands.*

6.5 Complexes of 4-Allyloxypyridine

With silver(I) perchlorate (**6.20**)

A crystalline compound resulting from the reaction of silver(I) perchlorate and ligand **6.12** occurred under the same reaction conditions as for the previously described complexes. X-ray analysis revealed the structure to be a one-dimensional metallopolymer

which solved in the orthorhombic space group Pbca. The asymmetric unit, seen in Figure 6.20, is similar to **6.16**, **6.17** and **6.18** in that it has one organic ligand, one silver atom and one counter anion.

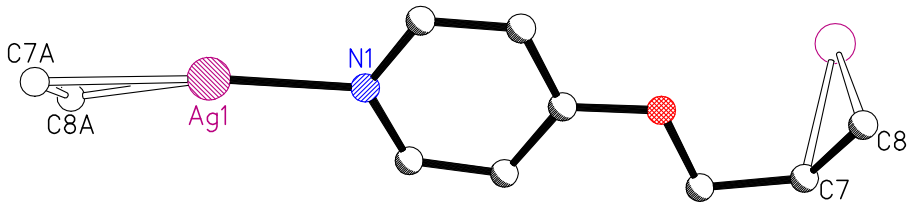
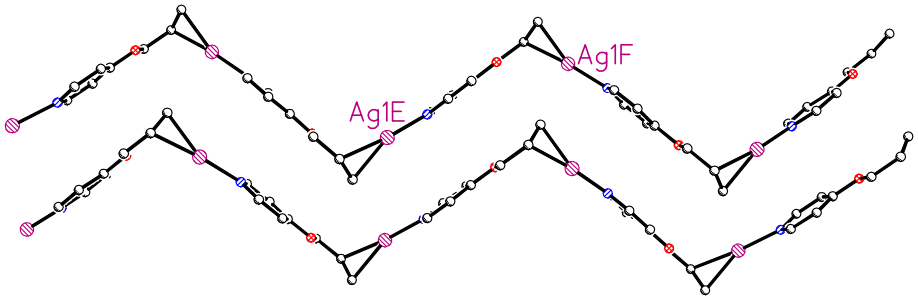


Figure 6.20 *– The asymmetric unit of* ***6.20****. Perchlorate anion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.175(5), Ag1-C7A 2.357(7), Ag1-C8A 2.310(7), Ag1-C7A,C8A 2.237(7), N1-Ag1-C7A,C8A 165.6(3).*

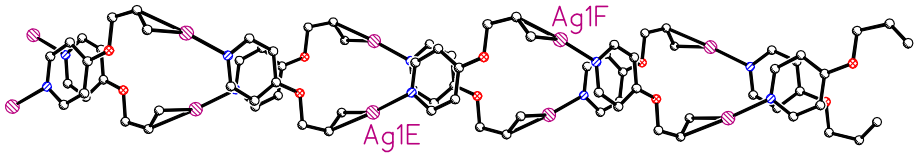
The silver atom is two coordinate with one alkene and one nitrogen atom bound. The geometry about the silver is almost linear with minor distortion (166 °) due to a weak interaction with one of the oxygen atoms from the perchlorate (2.71 Å). Ligand **6.12** bridges two silver atoms, one through the coordination of the pyridine nitrogen and to the other through the coordination of the alkene in the allyl ether arm. The change of the substitution pattern to *para* ligand **6.12** means it is no longer able to doubly bridge silver atoms in the same manner as **6.10** and **6.11** do. As expected the Ag···Ag separation across ligand **6.12**, Ag1F···Ag1E in Figure 6.21, is the longest seen in the allyloxypyridine series at a distance of 9.25 Å. This is around 1.5 Å longer than the separation shown by the *meta* isomer and about 5 Å longer than seen in the complexes with the *ortho* isomer.

Complex **6.20** is a one-dimensional zig-zag metallopolymer, as seen in Figure 6.21(a), with a 77.8 ° angle between the planes of adjacent pyridine rings. Individual polymers do not stack neatly on top of one another but cross back and forth, as shown in Figure 6.21(b), in an ABAB packing arrangement with π-π stacking between the pyridine rings. The perchlorate counter anions sit between polymer strands and weakly interact with two

silver atoms from adjacent polymer strands (2.71 and 2.73 Å). The perchlorate is also involved in weak hydrogen bonding between its oxygen atoms and the hydrogen atoms on the organic ligand (2.42 Å).



a)



b)

Figure 6.21 *– Sections of the metallopolymer* ***6.20****. Hydrogen atoms have been omitted for clarity.* ***a)*** *View of the zig-zag nature* ***b)*** *view of two polymer strands crossing over one another, where every second strand is in the same orientation.*

With silver(I) hexafluorophosphate (**6.21**)

The product from the reaction of silver(I) hexafluorophosphate with **6.12**, under the same conditions described previously, is isomorphous to **6.20**. Compound **6.21** was analysed by X-ray crystallography and solved in the same space group, orthorhombic Pbca, with very similar cell dimensions to **6.20**. As in **6.20**, the asymmetric unit of **6.21**, shown in Figure 6.22, contains one silver atom, one organic ligand **6.12** and a non-coordinating counter anion.

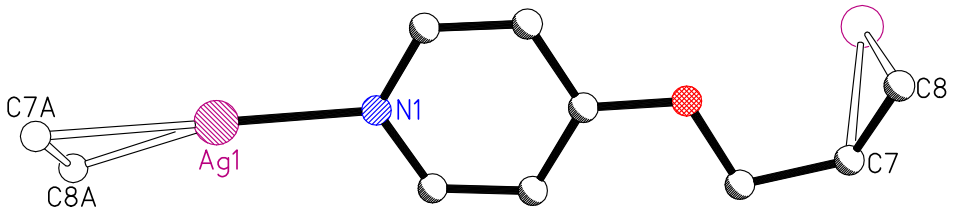


Figure 6.22 *– The asymmetric unit of* ***6.21****. Hexafluorophosphate anion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.152(4), Ag1-C7A 2.369(5), Ag1-C8A 2.275(5), Ag1-C7A,C8A 2.225(5), N1-Ag1-C7A,C8A 172.2(2).*

The silver is two coordinate with one alkene and one nitrogen bound with an almost linear geometry that has less distortion (172 °) than in **6.20**. This is probably due to the interaction between silver and a fluorine atom in the hexafluorophosphate anion being weaker (2.79 Å). The Ag···Ag separation is fractionally shorter than in **6.20** at 9.18 Å. Again ligand **6.12** bridges two silver atoms by the coordination of the pyridine nitrogen to one and the coordination of the alkene to the second.

Complex **6.21** forms a one-dimensional zig-zag polymer like **6.20** with the angle between the planes of adjacent pyridine rings closer to right angles (86.2 °). Individual polymers pack in the similar criss-crossing manner to **6.20** and the hexafluorophosphate counter anion sits between polymer strands enabling weak interactions between fluorine atoms on the anion and silver atoms from different polymer strands (2.79 and 2.88 Å). The counter anion is also involved with a series of weak hydrogen bonds with hydrogen atoms on **6.12** (2.44 - 2.65 Å).

6.6 Complexes of 2,6-Di(allyloxy)pyridine

With silver(I) perchlorate (**6.22**)

Ligand **6.13** was combined with silver(I) perchlorate in the same manner as the previous complexes and evaporation of all the solvents led to a crystalline product **6.22**. Complex **6.22** was analysed by X-ray diffraction and solved in the monoclinic space group C2/c.

The resulting structure has a 3:2 metal to ligand ratio with one and a half silver atoms in the asymmetric unit. The asymmetric unit, seen in Figure 6.23, also contains one full molecule of **6.13**, one full coordinated perchlorate anion and one half of a non-coordinated perchlorate.

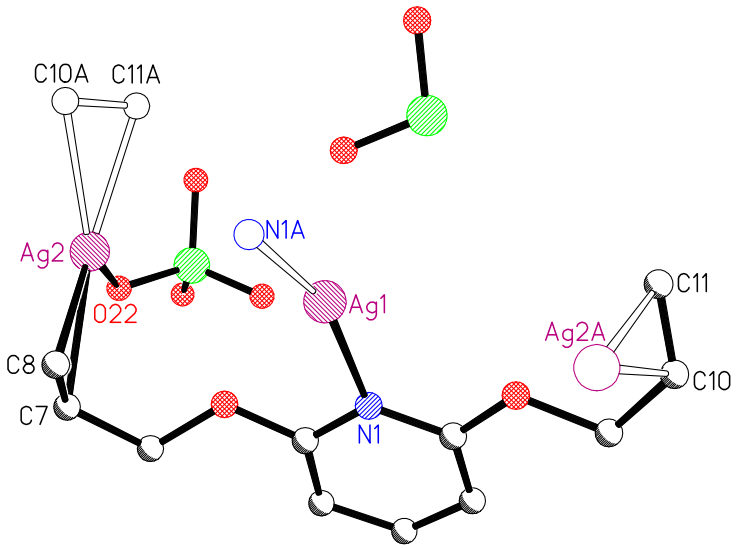
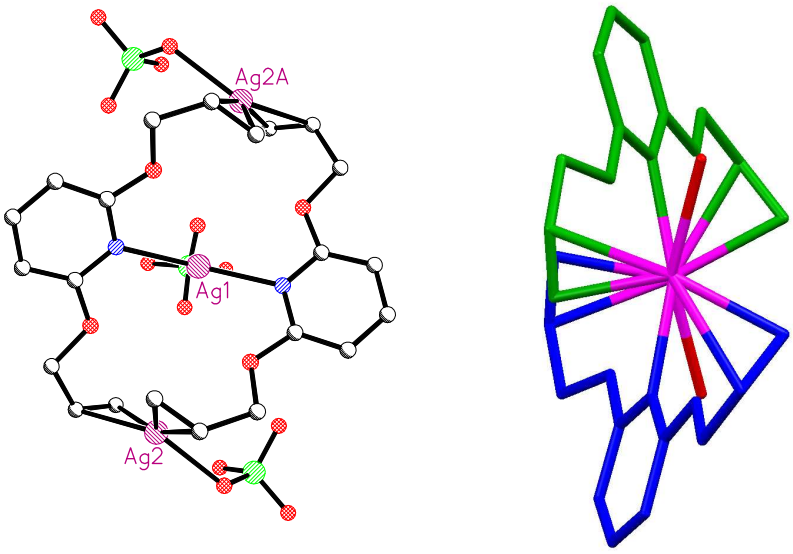


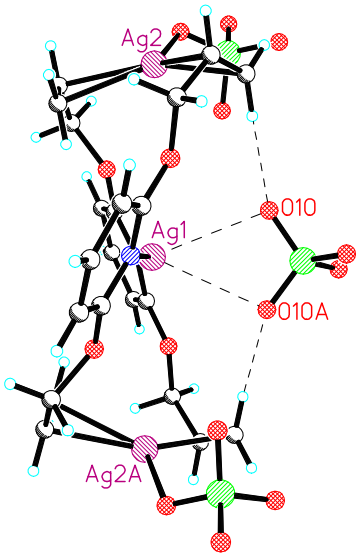
Figure 6.23 *– View of the asymmetric unit of* ***6.22****, hydrogen atoms are not displayed for viewing purposes. Selected bond lengths (Å) and angles (°): Ag1-N1 2.198(4), Ag2-C7 2.409(6), Ag2-C8 2.367(5), Ag2-C7,C8 2.293(6), Ag2-C10 2.442(6), Ag2-C11 2.329(6), Ag2-C10A,C11A 2.293(6), Ag2-O22 2.363(4), N1-Ag1-N1A 158.8(2), C7,C8-Ag2-O22 105.2(2), C10A,C11A-Ag2-O22 117.4(2), C7,C8-Ag2-C10A,C11A 137.2(2).*

The first silver atom, Ag1, lies on a two-fold rotation axis and is two coordinate with two heterocyclic nitrogen atoms coordinated. It has a distorted linear geometry with an angle of 159 °. The distortion arises from the close proximity of the non-coordinated perchlorate anion to Ag1 where two of its oxygen atoms weakly interact (2.85 Å) with Ag1. The second silver atom, Ag2, is three coordinate with two alkenes coordinated as well as one oxygen atom from a second perchlorate counter anion. It has distorted trigonal planar geometry with the biggest angle between the two alkene moieties. The

Ag···Ag distance between Ag1 and Ag2 is 4.35 Å, which is comparable to the Ag···Ag separation of 4.12 – 4.25 Å seen in the complexes with the structurally related ligand **6.10**.



a)



b)

Figure 6.24 *– View of the trinuclear, double-stranded helicate.* ***a)*** *Showing the helical nature of* ***6.22*** ***b)*** *showing the non-coordinated perchlorate weakly interacting with the helicate.*

Ligand **6.13** is tridentate coordinating to three silver atoms, two through the alkene groups and the third through the pyridine nitrogen. This structure is unique in this series in that it is the only example where each silver atom has only one type of functional group bound i.e. Ag1 has only nitrogen atoms coordinated and Ag2 has only alkenes coordinated. Previously both a nitrogen and an alkene were coordinated to the same silver atom.

Overall the structure is a discrete trinuclear, double-stranded helicate shown in Figure 6.24(a). The helicate is additionally classified as unsaturated[180] as it has two counter anions coordinated. Ligand **6.13**, in this context, acts as a heterotopic ligand with three monodentate binding domains. Complex **6.22** is a mixture of P and M helicies as is required by the fact that the structure solved in a centrosymmetric space group.

The non-coordinating perchlorate is further held in place by additional weak hydrogen bonding between O10 and O10A and the terminal olefinic hydrogen atoms (2.32 Å) as shown in Figure 6.24(b). The discrete M_3L_2 helicates interact with each other through C-H/π interactions between the pyridine ring and a methylene hydrogen atom (2.83 Å) and there are numerous weak hydrogen bonds between the perchlorate counter anions and the hydrogen atoms (2.49 – 2.70 Å) on ligand **6.13**.

With copper(I) chloride (**6.23**)

With unsuccessful attempts at inducing copper-alkene interactions with copper(I) iodide, complexes of ligands **6.10**, **6.11**, **6.12** and **6.13** with copper(I) chloride and copper(I) bromide were attempted through the *in situ* reduction of the copper(II) analogue. A literature procedure[181] was adopted involving the chosen ligand being mixed with the copper(II) salt dissolved in 2 mL of methanol in a 1:1 ratio. A freshly prepared triethylphosphite/methanol solution was added with enough volume to equal a three-fold excess of triethylphosphite. If the resulting solution was not colourless within five minutes of mixing further triethylphosphite was added drop-wise until the solution was colourless. The volume of methanol was reduced by half and diethyl ether was allowed to

diffuse into the solution. The copper(I) salt was stable under these conditions for about a week before significant amounts were oxidised back to copper(II).

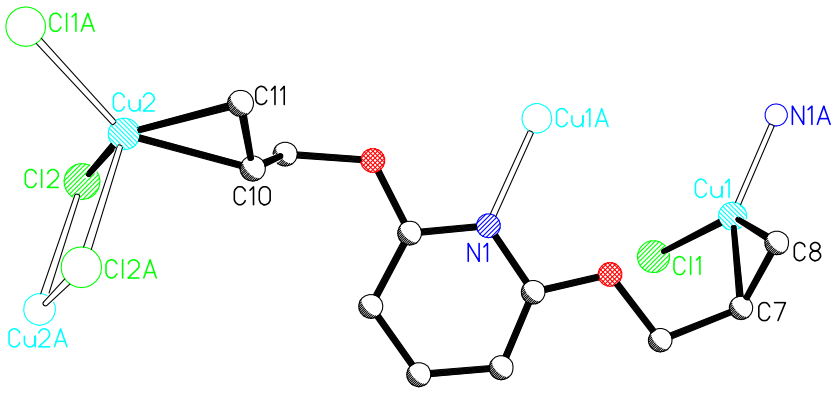


Figure 6.25 *- View of the asymmetric unit of* ***6.23****; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1-N1A 2.014(5), Cu1-C7 2.080(6), Cu1-C8 2.048(6), Cu1-C7,C8 1.949(6), Cu1-Cl1 2.262(2), Cu2-C10 2.086(6), Cu2-C11 2.063(7), Cu2-C10,C11 1.959(7), Cu2-Cl1 2.311(2), Cu2-Cl2 2.263(2), Cu2-Cl2A 2.744(2), N1-Cu1-Cl1 114.3(2), N1-Cu1-C7,C8 123.1(2), Cl1-Cu1-C7,C8 122.6(2), Cl1-Cu2-C10,C11 123.2(2), Cl2-Cu2-C10,C11 121.3(2), Cl2A-Cu2-C7,C8 92.9(2), Cl1-Cu2-Cl2 99.08(6), Cl2-Cu2-Cl2A 104.71(6).*

The only ligand to meet with success was **6.13** where very small colourless crystals were isolated when combined with copper(I) chloride. A single crystal was analysed by X-ray diffraction and a solution was obtained in the triclinic space group P-1. Unlike the silver(I) analogue with ligand **6.13** the metal to ligand ratio in **6.23** is 2:1 where the asymmetric unit contains, as shown in Figure 6.25, two copper atoms, one molecule of **6.13** and two chloride counter anions.

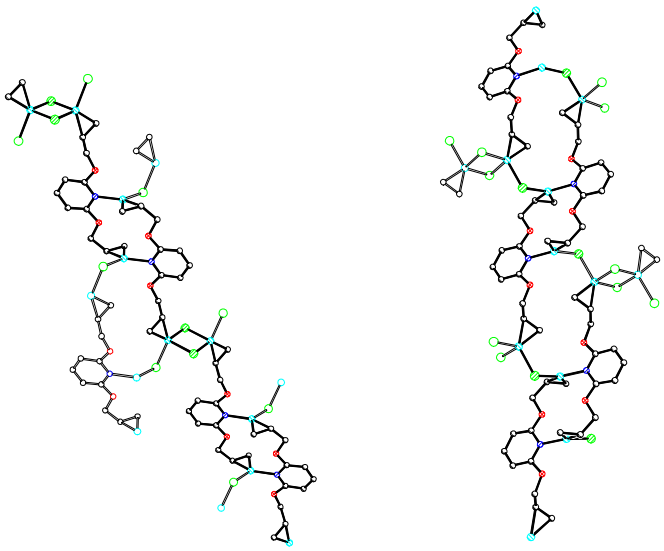
Ligand **6.13** is tridentate, as in the silver(I) analogue, coordinating to three copper atoms through both alkene groups and the pyridine nitrogen. This complex successfully demonstrates the ability of an alkene to coordinate to copper(I) reproducing other such results in the literature.[110,173]

There are two crystallographically independent copper atoms where one, Cu1, is three coordinate copper and is other, Cu2, is four coordinate. Cu1 has one pyridine nitrogen, one alkene and one chloride anion coordinated in a mildly distorted trigonal planar geometry. Alternatively, Cu2 has one alkene and three chloride anions coordinated with a calculated τ_4 of 0.82 indicating trigonal pyramidal geometry. Of the three chloride anions coordinated to Cu2 two of them, Cl2 and Cl2A, bridge to a second symmetry equivalent copper, Cu2A, to form a Cu_2Cl_2 unit. Within the unit, each copper has one short Cu-Cl bond of 2.26 Å and one long Cu-Cl bond of 2.74 Å making it rectangular rather than square. Interestingly, within **6.23** the Cu-C distances, 2.05 – 2.08 Å, are similar to the Cu-N bond length of 2.01 Å with the distance between the copper and the olefinic centroid being slightly shorter at 1.95 Å and 1.96 Å. Also the double bond is longer in the copper(I) complex with C=C of 1.359(9) Å and 1.366(9) Å than in the silver(I) complex which has C=C bond lengths of 1.335(8) Å and 1.319(9) Å. The ethereal oxygen atoms in **6.13** are not coordinated to the copper.

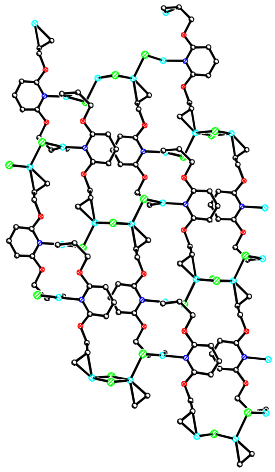
The Cu···Cu separation between Cu1A and Cu1, in Figure 6.26, is 4.30 Å which is very similar to the Ag···Ag separation of 4.35 Å seen in complex **6.22**. However the Cu···Cu separation between Cu1A and Cu2 is significantly longer at 6.99 Å which is due to the flexibility in the allyl ether arm allowing it to adopt a different conformation.

As opposed to discrete M_3L_2 helicates, ligand **6.23** forms a complicated two-dimensional metallopolymer when reacted with copper(I). The metallopolymer has some structural similarities to the silver complex **6.17** with ligand **6.10** in that M_2L_2 macrocycles are formed with the same bonding motif. One dimension of the polymer is propagated by the extra allyl ether arm in ligand **6.13** linking the M_2L_2 units to Cu_2Cl_2 fragments in an alternating fashion as seen Figure 6.26(a). The second direction of polymer propagation arises from the extra allyl ether arm forming a second larger macrocycle, which is very similar to the M_2L_2 macrocycle, but now includes an extra CuCl. The two alternating macrocycles give rise to the second direction as shown in Figure 6.26(b). A complete section of the two-dimensional metallopolymer is shown in Figure 6.26(c) which displays

offset π-π stacking between pyridine rings. There are no significant interactions between the two-dimensional sheets of the metallopolymer.



a) ***b)***



c)

Figure 6.26 *– Building up the two dimensions of* ***6.23****.* ***a)*** *Showing polymer propagation in one direction* ***b)*** *showing second direction of propagation* ***c)*** *showing a complete section of the two-dimensional metallopolymer. Hydrogen atoms have excluded for clarity.*

6.7 Complexes of N-Allyl-2-pyridone

With silver(I) triflate (**6.24**), hexafluorophosphate (**6.25**) and perchlorate(**6.26**)

A series of three complexes were formed with ligand **6.14** when combined with silver(I) triflate **6.24**, hexafluorophosphate **6.25** and perchlorate **6.26**. Each complex was made in the same manner which involved mixing a chloroform solution of the ligand with an acetone solution of the appropriate silver(I) salt in a mole ratio of 1:1, then followed by diethyl ether vapour diffusion. Both **6.25** and **6.26** solved in the monoclinic space group $P2_1/c$ and **6.24**, having significantly different cell dimensions, solved in the triclinic space group P-1.

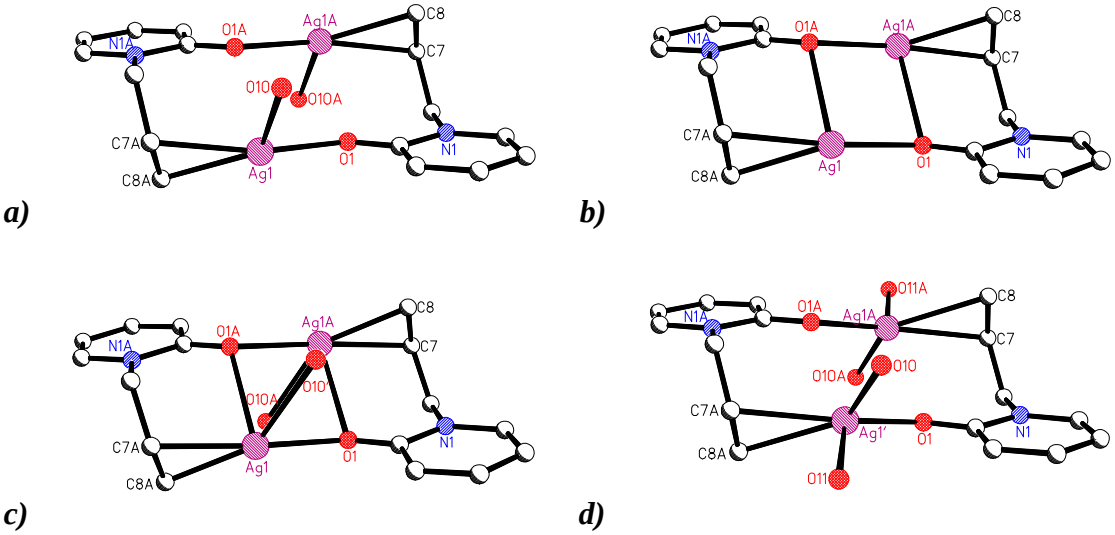


***Figure 6.27** – Comparison of M_2L_2 units of complexes **6.24**, **6.25** and **6.26**. For clarity only the coordinated oxygen atoms from the counter anion is displayed and hydrogen atoms have been omitted. **a)** Showing complex **6.24** with silver in the position of 95 % occupancy **b)** showing complex **6.25** **c)** showing complex **6.26** with silver in the position of 77 % occupancy, Ag1 **d)** showing complex **6.26** with silver in the position of 23 % occupancy, Ag1' .*

	6.24 (Å)	**6.25** (Å)	**6.26** (Å)
Ag1-O1	2.226(2)	2.195(1)	2.238(3)
Ag1-O1A	N/A	2.596(1)	2.527(3)
Ag1-C7	2.401(3)	2.390(2)	2.313(4)
Ag1-C8	2.376(4)	2.363(2)	2.242(5)
Ag1-C7,C8	2.294(4)	2.279(2)	2.177(5)
Ag-O10	2.485(4)	N/A	N/A
Ag-O10'	N/A	N/A	2.585(8)

***Table 6.1** – Selected bond lengths from complexes **6.24**, **6.25** and **6.26**. Only the dominant silver atom and counter anion occupancy in **6.26** is included.*

	6.24 (°)	**6.25** (°)	**6.26** (°)
O1-Ag1-C7A,C8A	152.0(2)	161.7(1)	159.8(1)
O1A -Ag1-C7A,C8A	N/A	79.9(1)	86.8(1)
O1-Ag1-O1A	N/A	93.3(1)	92.7(1)
O10-Ag1-C7A,C8A	105.0(1)	N/A	N/A
O1-Ag1-O10	98.6(1)	N/A	N/A
O1-Ag1-O10'	N/A	N/A	70.5(2)
O1A-Ag1-O10'	N/A	N/A	70.2(2)
O10'-Ag1-C7A,C8A	N/A	N/A	127.6(2)

***Table 6.2** – Selected bond angles from complexes **6.24**, **6.25** and **6.26**. Only the dominant silver atom and counter anion occupancy in **6.26** is included.*

The basic content of the asymmetric unit is the same for each complex with each containing one molecule of ligand **6.14**, one silver atom and one counter anion. All three complexes are made up of the same basic M_2L_2 unit which is similar in nature to the one formed with ligand **6.10** and silver(I). However in this instance it is the carbonyl oxygen atom that is coordinating to the silver as opposed to the nitrogen atom in **6.16** and **6.17**. Ligand **6.14** bridges two silver atoms by the coordination of the carbonyl oxygen to one silver and coordination of the alkene to the second. The distance between the centroid of the double bond and the silver atom in this series is shorter, consistent with what was observed in the allyloxypyridine complexes.

In both complexes **6.24** and **6.25** the silver atoms are three coordinate with distorted T-shaped geometry. Each silver atom has one alkene and one carbonyl oxygen atom coordinated as well as a second carbonyl oxygen in **6.25** and an oxygen from the counter anion in **6.24**. In complex **6.24** the silver is disordered over two positions with one being the dominant with 95% occupancy. In this position the Ag···Ag separation is 3.61 Å and in the minor position the oxygen from the triflate anion is no longer coordinating and the Ag···Ag separation has contracted slightly to 3.55Å. The Ag···Ag separation in complex **6.25** is even shorter at 3.30 Å.

Complex **6.26** is more complicated than the previous two as the silver is also disordered over two positions and the oxygen atoms surrounding the chlorine in the perchlorate are disordered over three positions. The dominant silver position with 77 % occupancy, Ag1 in Figure 6.27(c), has one oxygen from the counter anion coordinating in two positions of the perchlorate disorder totalling 50 % occupancy. The second silver position, Ag1' in Figure 6.27(d), has two oxygen atoms from the counter anion coordinating in two positions of the perchlorate disorder totalling 75 % occupancy. When the silver is in the Ag1' position and the oxygen atoms from the perchlorate are in coordinating positions, the structure is a two-dimensional sheet with the perchlorate bridging the M_2L_2 units in two directions.

In all three complexes, the discrete units pack together with numerous weak hydrogen bonding interactions between hydrogens on the organic ligand and; fluorines on the hexafluorophosphate in **6.25**, fluorine and oxygen atoms on the triflate in **6.24** and oxygens on the perchlorate in **6.26**.

6.8 Mixed Metal Compounds

Attempts were made to produce mixed metal architectures by using a ligand that would bridge two different metals. In particular, ligand **6.2** was targeted as it could coordinate to a non-silver transition metal through the heterocyclic nitrogen atom and then coordinate to silver(I) through the alkene. A simplistic approach was used initially where three

components were combined together in one step. Initial solutions were made up of silver(I) perchlorate in acetone, **6.2** in dichloromethane and either; copper(II) nitrate, cobalt(II) nitrate or nickel(II) nitrate dissolved in acetone, in a 1:2:1 ratio. Anion exchange occurred in both the copper and nickel samples leading to the precipitation of silver(I) nitrate. The cobalt solution resulted in the previously known one-dimensional metallopolymer, shown in Figure 6.5, which only contains silver(I) perchlorate and ligand **6.2**.

A step wise approach was tried next, where the non-silver metal salt was mixed with ligand **6.2**, in the same solvent conditions and ratios as the previous experiment, and left for a week. Silver(I) perchlorate, dissolved in acetone, was then added and the solvents were left to slowly evaporate. The solutions containing copper(II) nitrate and nickel(II) nitrate gave the same results, solid silver(I) nitrate, but the cobalt(II) nitrate solution gave a new complex (**6.27**) of ligand **6.2** with silver(I) nitrate.

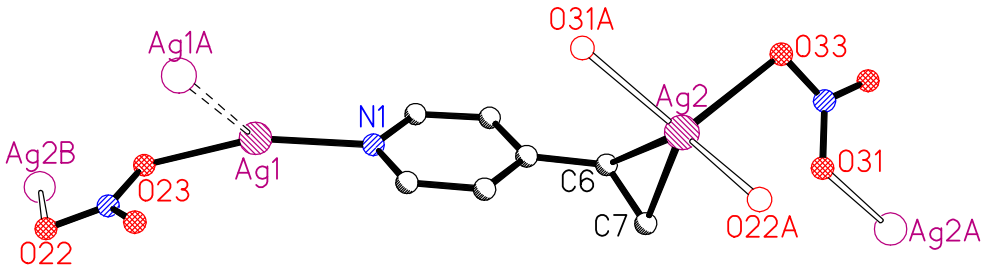


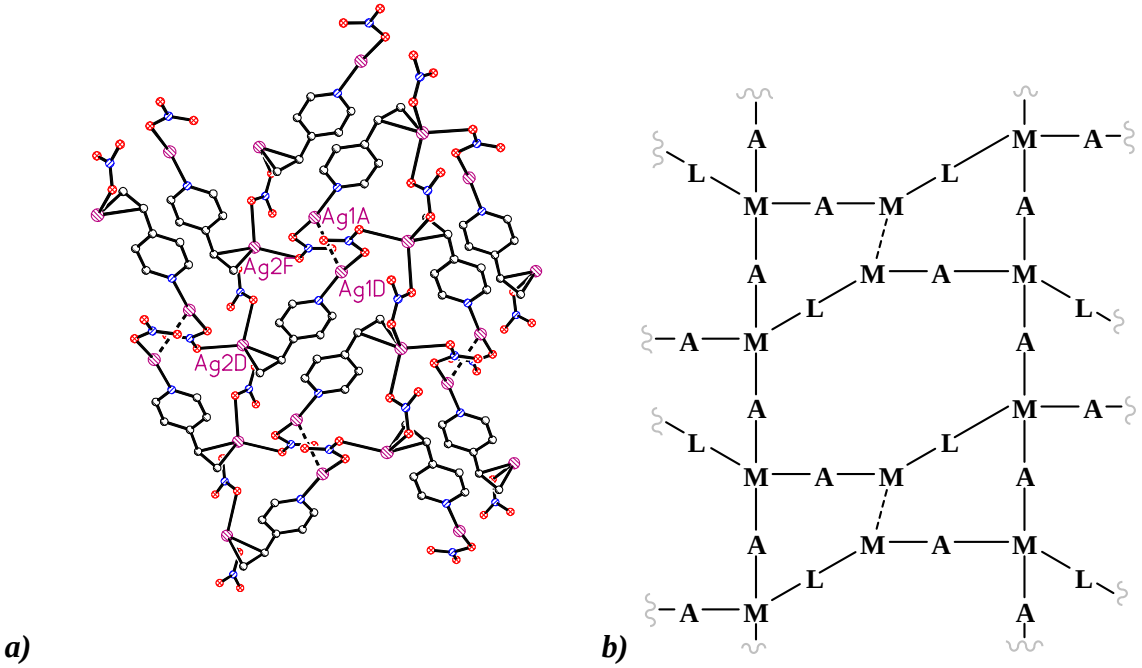
Figure 6.28 *– Asymmetric unit of* ***6.27****. Hydrogen atoms and silver disorder has been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-Ag1A 3.070(3), Ag1-N1 2.181(2), Ag1-O23 2.229(2), Ag2-C6 2.539(2), Ag2-C7 2.400(2), Ag2-C6,C7 2.377(2), Ag2-O22A 2.407(2), Ag2-O31A 2.449(2), Ag2-O33 2.535(2), N1-Ag1-O23 162.0(1), O22A-Ag2-O31A 107.21(6), O22A-Ag2-O33 103.27(6), O31A-Ag2-O33 111.23(6), O22A-Ag2-C6,C7 124.31(7), O31A-Ag2-C6,C7 109.54(7), O33-Ag2-C6,C7 100.64(7).*

Complex **6.27** solved in the monoclinic space group $P2_1/c$ and has two symmetrically independent silver atoms in the asymmetric unit: Ag1 and Ag2. Ag1 is disordered over two positions with only the dominant occupancy (78 %) shown in Figure 6.28. Coordinated to Ag1 are a pyridine nitrogen and an oxygen from the nitrate counter anion giving a slightly bent geometry (162.0 °). Ag1 is in close proximity to a second symmetry equivalent silver atom Ag1A. The Ag···Ag separation is of a medium distance at 3.07 Å and the slightly bent geometry of Ag1 is an indicator that the interaction is bonding. Ag1 does not have any alkenes coordinated. The second type of silver atom, Ag2, is four coordinate with a calculated τ_4 value of 0.88 indicating a geometry between tetrahedral and trigonal pyramidal. Ag2 has one alkene and three oxygen atoms from different nitrate counter anions coordinated and does not have any nitrogen atoms coordinated.

The ligand **6.2** bridges Ag1 and Ag2 by coordinating to one silver via the heterocyclic nitrogen and to the other through the alkene. The nitrate counter anions also act as bridging ligands connecting Ag2 to Ag2A and also Ag2B to Ag1 as shown in Figure 6.28.

Complex **6.27** is a two-dimensional metallopolymer. One direction of propagation is comprised of a silver nitrate backbone through symmetrically equivalent silver atoms, Ag2F and Ag2D, bridged by nitrate counter anions as shown in Figure 6.29(a). These silver nitrate chains are linked to each other through ligand **6.2** bridging to the second type of silver, Ag1D, which is in turn bridged by a nitrate anion to the next silver nitrate chain.

The Ag···Ag separation across ligand **6.2** in complex **6.27**, Ag2D and Ag1D in Figure 6.29(a), is 7.92 Å which is comparable to the Ag···Ag separation of 7.74 Å seen in the complex of **6.2** with silver(I) perchlorate. Not surprisingly this is shorter than the Ag···Ag separation of 9.15 - 9.25 Å displayed by ligand **6.12** which has two additional spacer atoms.



a) ***b)***

Figure 6.29 *– Selected silver–silver distances: Ag2D···Ag1D 7.92 Å Ag2F···Ag2D 5.23 Å, Ag2F···Ag1A 4.88 Å.* ***a)*** *View of the two-dimensional network* ***b)*** *a schematic view of the two-dimensional network, M = Ag^{+}, L =* ***6.2****, A = nitrate.*

Two-dimensional sheets interact with each other through weak anion silver interactions as well as weak hydrogen bonding between an aromatic hydrogen and an oxygen atom on the nitrate (2.52 Å) with an additional weak hydrogen bond between an olefinic hydrogen on **6.2** and an oxygen on the nitrate (2.51 Å).

To prevent the silver(I) ions precipitating as silver(I) nitrate, copper(II) perchlorate was next used instead of copper(II) nitrate. A solution of all three components, copper(II) perchlorate, ligand **6.2** and silver(I) perchlorate, was made in the same manner as previously described. The silver(I) ions stayed in solution however slow evaporation yielded the previously identified one-dimensional polymer with silver(I) perchlorate and **6.2**. This led to the conclusion that a stepwise synthesis is needed with the first step involving the creation of metal-centred ligand with a relatively non-labile transition metal.

Palladium was chosen as it is semi-labile and has well a defined coordination chemistry, preferring a four coordinate square-planar geometry. The target was to have four molecules of **6.2** coordinated to a central palladium atom. To achieve this, dichlorobisbenzonitrile palladium was dissolved in chloroform and added to a chloroform solution with two equivalents of **6.2**. The solution was stirred overnight which gave a bright yellow precipitate of dichlorobis-4-vinylpyridine palladium (**6.28**). To a suspension of **6.28** in acetone silver(I) perchlorate was added to strip the chlorine atoms as AgCl. This process took a couple of days to complete and once finished the mixture is filtered giving a clear yellow solution. The solvent was reduced and a further two equivalents of **6.2** in chloroform was added. Diethyl ether diffusion and evaporation of the solvent gave the target metal-centred ligand **6.29**. This ligand crystallised into two different space groups dependent on the orientation of the vinyl groups of the coordinated **6.2**.

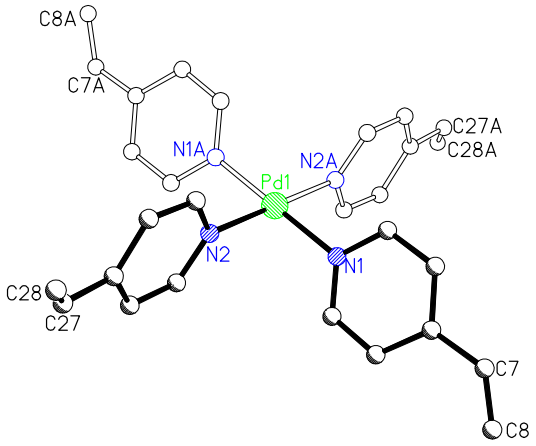


Figure 6.30 *– The asymmetric unit of the metal-centred ligand* ***6.29*** *in the space group R-3. Hydrogen atoms and counter anions have been removed for clarity. Selected bond lengths (Å) and angles (°): Pd1-N1 2.023(4), Pd1-N2 2.024(5), N1-Pd1-N1A 179.995(1), N1-Pd1-N2 89.4(2), N2-Pd1-N2A 179.996(1).*

The first space group, R-3, is of high symmetry and there is only one half molecule of **6.29** and one perchlorate counter anion in the asymmetric unit. The palladium is four

coordinate with square-planar geometry and sits on a centre of inversion. Two of the ligands have the vinyl group pointing ‘down’ and two of the ligands have the vinyl group pointing ‘up’ in a down, down, up, up arrangement seen in Figure 6.30. The two perchlorate anions sit so that one of its oxygen atoms is directly above or below the palladium centre (3.09 Å) in a Jahn-Teller like conformation.

The second space group that **6.29** crystallises in is the low symmetry P-1. In the asymmetric unit there are now one and a half molecules of **6.29** and three perchlorate counter anions. Both palladiums are four coordinate with square-planar geometry and one palladium, Pd2, is sitting on a centre of inversion. The ligands surrounding Pd2 have the same down, down, up, up arrangement of the vinyl groups as in R-3 but Pd1 has a different arrangement with the vinyl groups in a down, down, down, up conformation.

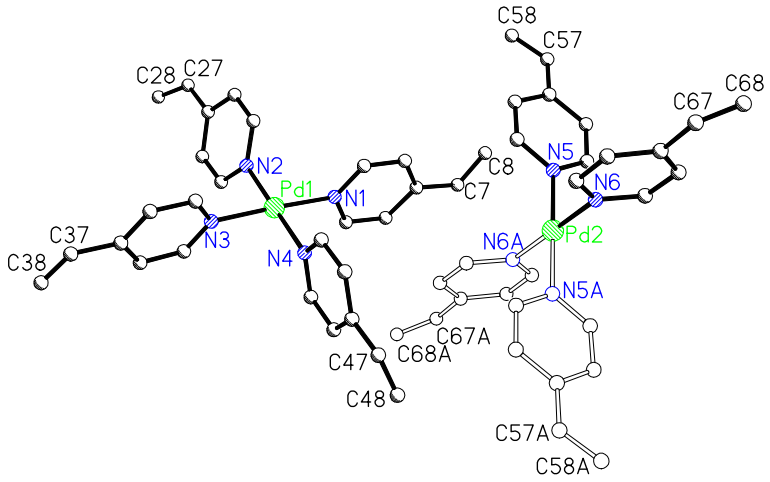
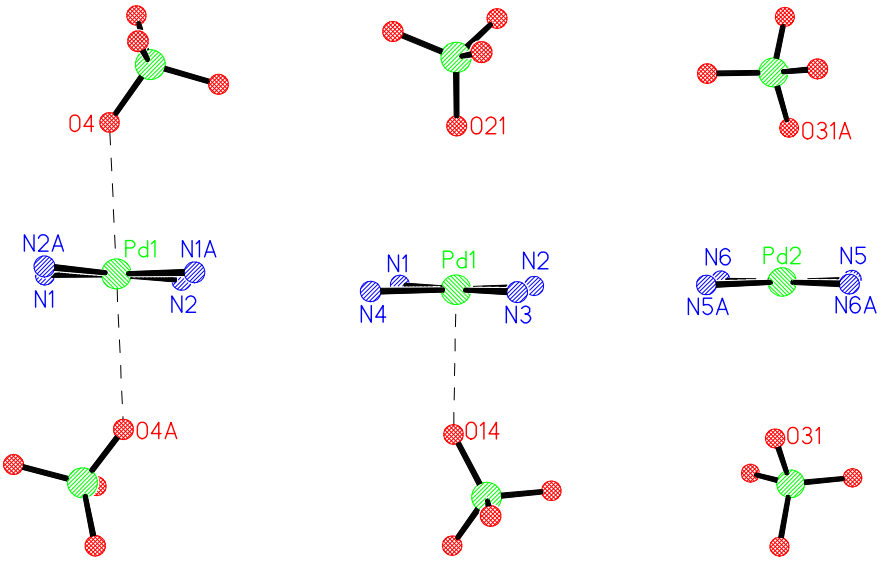


Figure 6.31 *- The asymmetric unit of the metal-centred ligand* ***6.29*** *in the space group P-1. Hydrogen atoms and counter anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-N1 2.012(4), Pd1-N2 2.019(4), Pd1-N3 2.031(4), Pd1-N4 2.025(4), Pd2-N5 2.028(4), Pd2-N6 2.014(4), N1-Pd1-N2 89.8(2), N1-Pd1-N3 177.8(2), N1-Pd1-N4 89.2(2), N2-Pd1-N3 91.2(2), N2-Pd1-N4 178.4(1), N3-Pd1-N4 89.7(2), N5-Pd2-N6 90.6(2), N5-Pd2-N6A 89.4(2), N5-Pd1-N5A 180.000(1), N6-Pd2- N6A 179.998(1).*

The two perchlorate anions again sit so that one of their oxygen atoms are above and below a palladium atom. Pd2 has the two oxygen atoms equidistant at 3.29 Å, a greater distance than seen in the R-3 structure. The two oxygen atoms above and below Pd1 are not equidistant with a shorter distance of 2.96 Å as in the R-3 structure, and a longer distance of 3.29 Å as in Pd2. A comparison of the positions of the perchlorate counter anions is shown in Figure 6.32.



a) **b)** **c)**

Figure 6.32 *– Comparison of the environment surrounding palladium, dashed line indicates a shorter Pd···O distance.* ***a)*** *Palladium environment in R-3* ***b)*** *environment of Pd1 in P-1* ***c)*** *environment of Pd2 in P-1.*

Both crystal structures had void space which had significant residual electron density which was suspected to be, in both cases, disordered diethyl ether. As this was not the object of study the SQUEEZE algorithm was used to remove the residual electron density.

Success in forming mixed metal compounds was not achieved with silver(I) and **6.29** as the silver(I) would rapidly decay and was not stable in the presence of **6.29**.

Attempts were made to synthesise a cobalt(III) centred ligand with **6.2**. A literature procedure for the formation of carbonatochlorotris(pyridine)cobalt(III)[182] was used by the replacing pyridine with **6.2** and the use of perchloric acid instead of hydrochloric acid. While the products could be characterised by ^{1}H NMR to some extent, full characterisation and further experimentation could not be completed as the products were not isolated from the reaction mixture.

6.9 Summary

This chapter details the synthesis of five bi-functional ligands **6.10**, **6.11**, **6.12**, **6.13** and **6.14**. These ligands are based around a pyridine core and contain, with the exception of **6.14**, both an alkene functional group and a nitrogen functionality. Ligand **6.14** contains a carbonyl oxygen, a tertiary nitrogen and an alkene functional group.

The coordination chemistry of ligands **6.10**, **6.11**, **6.12**, **6.13** and **6.14** with silver(I) was explored with a variety of salts, with coordinating or non-coordinating counter anions as well as with copper(I) chloride, bromide and iodide. A commercially available ligand **6.2** was used unsuccessfully in attempts to create a mixed metal system and also used, with success, in the formation of a palladium centred ligand, **6.29**. Thirteen new complexes were formed and studied by single crystal X-ray diffraction.

Ligands **6.10**, **6.11** and **6.14** displayed a preference for the formation of M_2L_2 units with silver(I). These units are either discrete, as in **6.16**, or linked together into a one-dimensional polymer by bridging anions as in **6.17**. Complex **6.18** is in between the two examples as the anion only weakly bridges M_2L_2 units. Ligand **6.12** acts as a simple bridging ligand and gives isomorphous one-dimensional polymers with silver(I) perchlorate **6.20** and silver(I) hexafluorophosphate **6.21**. **6.13** acts as a heterotopic ligand with three monodentate domains and forms a helicate with silver(I) perchlorate **6.22**. The helicate is classed as an unsaturated, trinuclear double-stranded helicate.

Two complexes with copper(I) were isolated; one with copper(I)-alkene interactions, **6.23**, and one without, **6.19**. Changing the metal from silver(I) to copper(I) changes the topology of the resulting assembly. Ligand **6.11** gave weakly linked M_2L_2 units with silver(I) perchlorate and resulted in a one-dimensional polymer when reacted with copper(I) iodide. Likewise ligand **6.13** gives a trinuclear double-stranded helicate with silver(I) perchlorate and when reacted with copper(I) chloride gives a two-dimensional polymer.

Silver(I), in the presence of ligands containing both alkene and pyridine functional groups, showed a marked preference, aside from counter anions, for the coordination of only one alkene and one nitrogen. Distances between silver and the centroid of the two olefinic carbons are generally shorter than seen in complexes in previous chapters. This is possibly due to there being only one alkene coordinated rather than two or three commonly seen in other series which reduces steric crowding enabling closer Ag-C distances. Further evidence that silver prefers to coordinate to an alkene over an ether oxygen is seen as there are no ethereal oxygen atoms interacting with silver in any of the complexes within this chapter.

Chapter Seven

Conclusion

CHAPTER 7

Conclusion

7.1 – Topology types.

The silver(I)-alkene synthon yielded a range of discrete and polymeric assemblies through the systematic exploration of different features of ligand design. A number of one-dimensional polymer topologies were formed including; linear, ladder, helical and necklace polymers. Two-dimensional metallopolymers were formed with topologies such as square grids, one-dimensional necklace polymers bridged into two dimensions and porous two-dimensional sheets. Three-dimensional polymers were also formed including an interpenetrated three-dimensional network. Discrete assemblies were also formed, of which the most common was the M_2L_2 macrocyclic unit. M_2L discrete units were also seen. A discrete unsaturated trinuclear, double-stranded helicate of the type M_3L_2 was formed as well as a M_4L_2 cage-like macrocycle.

7.2 - Silver(I) Coordination Sphere

Two coordinate

Within the work described in this thesis, there were two, three, four and five coordinate silver(I) atoms. Two coordinate silver(I) atoms are most often seen in combination with ligands that are bi-functional and additionally contain a heterocyclic nitrogen. Two coordinate silver(I) atoms arise when there is one heterocyclic nitrogen atom and one alkene coordinated. The silver to C=C centroid distance in these species is shorter which is presumably to do with steric repulsion between bulky groups. As there are fewer bulky groups around a two coordinate silver(I) atom, there is less repulsion, allowing closer distances. The geometry is often distorted from linear due to weak interactions with nearby counter anions.

Three coordinate

Three coordinate silver(I) atoms, within this thesis, have almost exclusively trigonal planar or distorted trigonal planar geometry. Most commonly, a three coordinate silver(I) atom has two olefins coordinated and the third coordination site is filled with an oxygen atom from a counter anion or solvent molecule. On occasions when an oxygen atom is not available, a third alkene or arene would fill the third coordination site. In such instances, the silver to C=C centroid distance is slightly longer. This is presumably from the steric repulsion of three bulky groups around a single silver(I) atom.

Four coordinate

There are two different types of four coordinate silver(I) atoms. In the first, silver(I) atoms have one alkene and three oxygen atoms, from various sources, coordinated and in the second, the silver(I) atoms have two alkenes and two oxygen atoms coordinated. When there is only one coordinated olefin the silver to C=C centroid distance is shorter and is comparable to distances in the two coordinate systems which also only have one olefin coordinated. The geometry of these types of four coordinate silver(I) atoms spans from see-saw to trigonal pyramidal to distorted tetrahedral.

In the complexes where there are two alkenes coordinated to a silver(I) atom, the silver to C=C centroid distance is of a medium length. They are comparable to distances in the three coordinate systems which also have two olefin moieties coordinated. The geometry of these four coordinate silver(I) atoms span from see-saw to trigonal pyramidal to distorted tetrahedral. Distortion from perfect geometries arises between the two oxygen atoms which almost always have the smallest angle, and between the two alkenes which in turn almost always have the largest angle.

Five coordinate

Five coordinate silver(I) atoms were rare with only two examples. In both instances, the silver was part of a one-dimensional silver(I)-anion cluster and there was only one example of a five coordinate silver(I) atom which had an alkene coordinated. This silver atom had four oxygen atoms and one olefin coordinated in a distorted square pyramidal

geometry. The silver to C=C centroid distance was shorter consistent with other examples of silver(I) atoms that have only one coordinated olefin.

7.3 – Future Directions

Within this work, the effect of the silver(I) to ligand ratio on the products was not systematically investigated. Whether the ratio has any influence may be gained from further investigation into the different silver(I) to ligand ratios. This work has also demonstrated that the counter anion can affect the outcome the reaction. This could be further explored using more exotic counter anions and also counter anions with a negative charge greater than one.

Mixed metal systems, in which the organic ligands have an olefinic binding domain specifically for silver(I) in addition to a heterocyclic binding domain for a second transition metal, are desirable targets. Further work in this area includes the fine tuning of metal-centred ligands to be compatible with silver(I). Lastly, the exploration of six armed ligands in this thesis has been of a limited scope and further ligands, such as hexaallylbenzene, would be a great addition to this body of work.

Chapter Eight

Experimental

CHAPTER 8

Experimental

8.1 General Experimental

^{1}H NMR spectra were recorded on Varian Unity 300 or Varian INOVA 500 spectrometers at 23 °C with a 3mm probe operating at 300 MHz or 500 MHz. ^{1}H NMR spectra recorded in $CDCl_3$ were referenced to solvent signals at 7.26 ppm and those recorded in deuterated acetone were referenced to solvent signals at 2.17 ppm. ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer at 23 °C with a 3mm probe operating at 75 MHz. ^{13}C NMR spectra recorded in $CDCl_3$ were referenced to solvent signals at 77.10 ppm. When required ^{1}H nOe, 1-D Tocsy and GHSQC experiments were performed using standard pulse sequences available with the Varian INOVA 500 system. Unless otherwise stated the value for chemical shifts is given to the centre of the multiplet. The ^{1}H NMR spectra for the ligands are denoted with primes to distinguish between the different aromatic rings or different olefinic hydrogens within the ligand.

Electrospray (ES) mass spectra were recorded using a Micromass LCT-TOF mass spectrometer, with the probe operating at 3200V and cone voltage of 30V. Samples were dissolved in methanol, and spectra acquired using source and desolvation temperatures of 80 °C and 150 °C respectively.

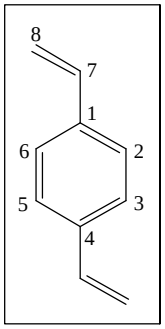
Melting points were recorded on a Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell microanalytical laboratory, University of Otago, Dunedin.

Unless otherwise stated, reagents were obtained from commercial sources and used as supplied. Solvents were purified by standard literature procedures and freshly distilled as required. The following compounds were prepared by literature procedures: 1,3,5-

trivinylbenzene,[108] 1,8-naphthalenediol,[134] tetra-O-allyl-pentaerythritol[167] 2-allyloxypyridine,[179] and 1,3,5-tri(allyloxy)benzene.[183]

8.2 Ligand Preparation

1,4-Divinylbenzene, ***1.28***

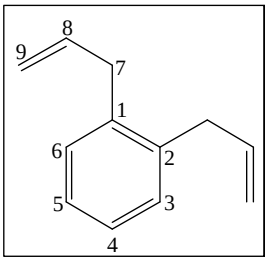


Ligand **1.28** was prepared using an adapted literature procedure.[184] Terephathalic aldehyde (0.610 g, 4.5 mmol) was dissolved in dioxane (40 mL with 0.6 mL water). Potassium carbonate (7 g) was added to the stirred solution along with methyl-triphenyl-phosphonium iodide (3.68 g, 9.1 mmol). The mixture was then refluxed while stirring for 20 hrs. This resulted in a mixture of mono and divinylbenzene. 1,4-Divinylbenzene was purified on an alumina column with petroleum ether. 2,6-Di-tert-butyl-4-methylphenol was added as a stabiliser as 1,4-divinylbenzene can spontaneously polymerise. Yield 0.112 g, 19 %. The proton ^{1}H NMR spectrum is comparable to literature values.[184] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (4H, s, H2, H3, H5, H6), 6.70 (2H, dd, *J* = 11.2, 17.6 Hz, H7), 5.75 (2H, d, *J* = 17.6 Hz, H8), 5.24 (2H, d, *J* = 11.2 Hz H8').

General procedure for the preparation of diallylbenzenes

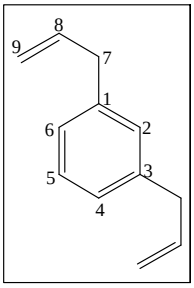
A solution of the appropriate dibromobenzene (0.354 g, 1.5 mmol), LiCl (25 mg, 0.6 mmol), tetrakis-(triphenylphosphine)palladium(0) (69 mg, 6 mol-%) and allyltributylstannane (1 mL, 3.3 mmol) in 10 mL anhydrous dioxane was heated at 100 °C under argon for 15 hours. After the reaction mixture was cooled to room temperature, 75 mL of dichloromethane was added and then extracted with 4×50 mL water. The solvent was then removed *in vacuo* and the residue was redissolved in diethyl ether (20 mL). To remove the tin residues the ether solution was vigorously stirred with 20 mL 20 % potassium fluoride. The organic layer was decanted off, dried (Na_2SO_4), filtered, and evaporated *in vacuo*. The product was then purified by chromatography on silica gel with petroleum ether as eluent.

1,2-Diallylbenzene, ***2.4***



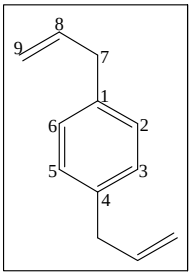
Ligand **2.4** was prepared using the general procedure and was isolated as a colourless oil. Yield 45.2 mg, 19 %. NMR data corresponds to literature values.[185] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (4H, s, H3, H4, H5, H6), 6.06-5.87 (2H, m, H8), 5.14-4.98 (4H, m, H9, H9'), 3.43 (4H, m, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 138.28, C1, C2; 137.40, C8; 129.91, C4, C5; 126.81, C3; C6; 116.05, C9; 37.40, C7.

1,3-Diallylbenzene, ***2.5***



Ligand **2.5** was prepared following the general procedure and was isolated as a colourless oil. Yield 150 mg, 63 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (1H, t, *J* = 7.5 Hz, H5), 7.11-6.98 (3H, m, H2, H4, H6), 5.99 (tdd, *J* = 6.8, 16.8, 10.1 Hz, H8), 5.24-4.95 (4H, m, H9, H9'), 3.39 (4H, d, *J* = 6.8 Hz, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 140.63, C1, C3; 137.79, C8; 129.12, C2; 128.75, C5; 126.60, C4, C5; 116.01, C9; 40.48, C7.

1,4-Diallylbenzene, ***2.6***



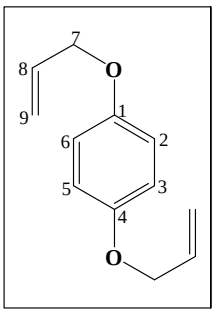
The title compound was prepared following the general procedure and was isolated as a pale yellow oil. Yield 0.230 g, 97 %. NMR data corresponds to literature values.[186] ^{1}H NMR (500MHz, $CDCl_3$): δ 7.15 (4H, s, H2, H3, H5, H6), 5.99 (2H, tdd, *J* = 6.7, 16.8, 10.0 Hz, H8), 5.13-5.07 (4H, m, H9, H9'), 3.39 (4H, td, *J* = 6.7, 1.3 Hz, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 138.02, C1, C4; 137.87, C8; 128.89, C2, C3, C5, C6; 115.91, C9; 40.12, C7.

General procedure for the preparation of di(allyloxy)benzenes

This method was adopted from a literature procedure.[107] Allyl bromide (1.74 mL, 20 mmol) was added drop-wise over 15 minutes to a mixture of the appropriate dihydroxybenzene (1.1 g, 10 mmol) and potassium carbonate (2.76 g, 20 mmol) in 60 mL acetone. The resulting solution was refluxed for 5 hrs and then filtered. The filtrate and

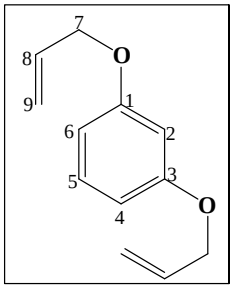
acetone washings were collected and the solvent removed *in vacuo*. The remaining oil was treated with 60 mL of 1 M NaOH and di(allyloxy)benzene was extracted with 3×75 mL petroleum ether. The organic extracts were combined and the solvent removed.

1,4-Di(allyloxy)benzene, ***2.9***



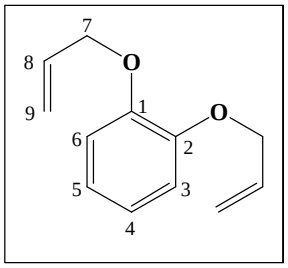
1,4-Di(allyloxy)benzene was prepared following the general procedure. The crude product was recrystallised from pentane. Yield 1.309 g, 69 %. M.p. 33-36 °C lit 36 °C[107]. NMR is consistent with literature values.[107] ^{1}H NMR (300MHz, $CDCl_3$): δ 6.84 (4H, s, H2, H3, H5, H6), 6.05 (2H, ddt, *J* = 17.08, 10.50, 5.32 Hz, H8), 5.39 (2H, dd, *J* = 17.24, 1.57 Hz, H9), 5.27 (2H, dd, *J* = 10.46, 1.36 Hz, H9'), 4.48 (4H, m, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 153.21, C1, C4; 133.95, C8; 117.72, C9; 115.94, C2, C3, C5, C6; 69.72, C7.

1,3-Di(allyloxy)benzene, ***2.8***



1,3-Di(allyloxy)benzene was prepared following the general procedure. The crude product was extracted from the resulting oil with pentane. No further purification was necessary. Yield 1.487 g, 78 %. Proton NMR is consistent with literature values.[187] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.08 (1H, m, H5), 6.53 (3H, m, H2, H4, H6), 6.07 (2H, ddt, *J* = 17.3, 10.5, 5.3 Hz, H8), 5.42 (2H, dq, *J* = 17.3, 1.6 Hz, H9), 5.29 (2H, dq, *J* = 10.5, 1.4 Hz, H9'), 4.52 (4H, dt, *J* = 5.3, 1.5 Hz, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.11, C1, C3; 133.57, C8; 130.14, C5; 117.96, C9; 107.45, C6, C4; 102.28, C2; 69.11, C7.

1,2-Di(allyloxy)benzene, ***2.7***



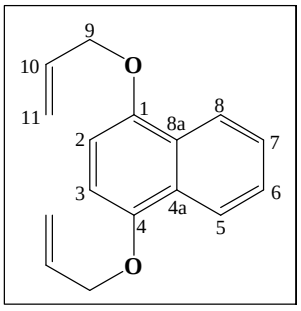
1,2-Di(allyloxy)benzene was prepared following the general procedure. The crude product was extracted from the resulting oil using pentane. No further purification was necessary. Yield 1.325 g, 70 %. NMR is consistent with literature values.[188] ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (4H, s, H3, H4, H5, H6), 6.10

(2H, ddt, *J* = 17.22, 10.6, 5.3 Hz, H8), 5.43 (2H, ddd, *J* = 17.5, 3.2, 1.5 Hz, H9), 5.28 (2H, dq, *J* = 10.4, 1.4 Hz, H9'), 4.62 (4H, dt, *J* = 5.1, 1.5 Hz, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 148.88, C1, C2; 133.86, C8; 121.55, C4, C5; 117.79, C9; 114.61, C3, C6; 70.21, C7.

General procedure for the preparation of di(allyloxy)naphthalenes

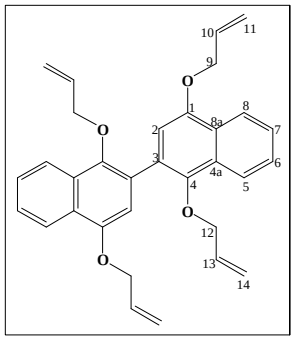
This method was adapted from a literature procedure.[107] Allyl bromide (0.44 mL, 5 mmol) was added drop-wise over 15 minutes to a mixture of the appropriate dihydroxynaphthalene (0.4 g, 2.5 mmol) and potassium carbonate (0.7 g, 5 mmol) in 25 mL acetone. The resulting mixture was refluxed for 5 hrs then filtered and washed with acetone. The filtrate and washings were allowed to cool to room temperature and then a 1 M solution of NaOH was added until the di(allyloxy)naphthalene crystallised out of solution.

1,4-Di(allyloxy)naphthalene, ***3.8***



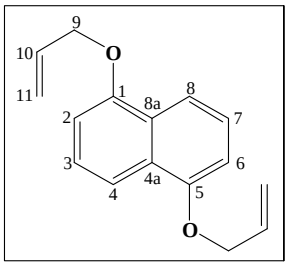
Purified by column chromatography with 2:100 ethyl acetate:petroleum ether, then recrystallised from petroleum ether. Yield 0.214 g, 36 %. M.p. 50 – 52 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (2H, dd, *J* = 6.4, 3.3 Hz, H5, H8), 7.51 (2H, dd, *J* = 6.4, 3.3 Hz, H6, H7), 6.71 (2H, s, H2, H3), 6.18 (2H, tdd, *J* = 5.2, 17.2, 10.4 Hz, H10), 5.52 (2H, ddd, *J* = 17.2, 3.2, 1.6 Hz, H11), 5.33 (2H, ddd, *J* = 10.5, 2.8, 1.4 Hz, H11'), 4.67 (4H, dt, *J* = 5.1, 1.5 Hz, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 148.80, C1, C4; 133.95, C10; 126.90, C5, C8; 126.13, C4a, C8a; 122.17, C5, C8; 117.47, C11; 105.04, C2, C3; 69.64, C7. Elem. Anal. found: C, 79.84; H, 6.54. Calc for $C_{16}H_{16}O_2$: C: 79.97 H: 6.71. ESI-MS: found M^+ = 240.1159; $C_{16}H_{16}O_2$ requires M^+ = 240.1150.

1,1',4,4'-Tetra(allyloxy)-2,2'-binaphthalene, ***3.15***



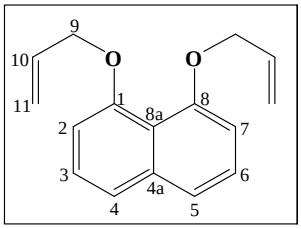
Compound **3.15** was isolated as a byproduct in the formation of ligand **3.8**. Yield 3.7 mg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (2H, d, *J* = 8.4 Hz, H5), 8.21 (2H, d, *J* = 8.2 Hz, H8), 7.62-7.49 (2H, m, H6, H7), 7.13 (2H, s, H2), 6.26-6.09 (2H, m, H10), 5.94-5.79 (2H, m, H13), 5.56-5.48 (2H, m, H11), 5.36-5.28 (2H, m, H11'), 5.25-5.18 (2H, m, H14), 5.12-5.05 (2H, m, H14'), 4.74-4.69 (4H, m, H9), 4.20 (4H, dd, *J* = 5.6, 1.2 Hz, H12). MH^+ = 479.2203; $C_{32}H_{30}O_4$ requires MH^+ = 479.2222

1,5-Di(allyloxy)naphthalene, ***3.9***



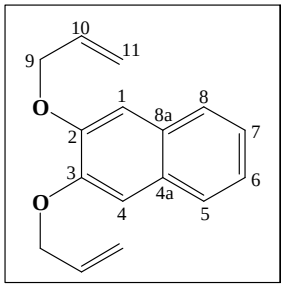
Allyl bromide (1.3 mL, 0.015 mol) was added drop-wise over 15 minutes to a mixture of 1,5-dihydroxynaphthalene (1.2 g, 7.5 mmol) and potassium carbonate (2.07 g, 0.015 mol) in 50 mL acetone. The resulting mixture was refluxed for 5 hrs then filtered and washed with acetone. The filtrate and acetone washings were collected and the solvent removed *in vacuo*. The remaining oil was treated with 45 mL of 1 M NaOH and 1,5-di(allyloxy)naphthalene was extracted with 3×75 mL diethyl ether. The organic extracts were combined and the solvent removed. The residue was redissolved in acetone 40 mL and 45 mL of 1 M NaOH was added where upon 1,5-Di(allyloxy)naphthalene crystallised out of solution. Further purification by recrystallistion from pentane gave a pale yellow crystalline solid. Yield 1.762 g, 95.4 %. M.p. 94 – 96 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (2H, d, *J* = 8.5 Hz, H4, H8), 7.37 (2H, t, *J* = 8.0 Hz, H3, H7), 6.86 (2H, d, *J* = 7.7 Hz, H2, H6), 6.18 (tdd, *J* = 5.1, 17.2, 10.4 Hz, H10), 5.53 (2H, dd, *J* = 17.3, 1.5 Hz, H11), 5.34 (2H, dd, *J* = 10.6, 1.3 Hz, H11'), 4.72 (4H, d, *J* = 5.1 Hz, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 154.09, C1, C5; 133.35, C10, 126.83, C4a, C8a; 125.07, C3, C7 117.30, C11, 114.49, C4, C8; 105.81, C2, C6; 68.95, C9. Elem. Anal. found: C, 74.96; H, 6.47. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. ESI-MS: found M^+ = 240.1152; $C_{16}H_{16}O_2$ requires M^+ = 240.1150.

1,8-Di(allyloxy)naphthalene, ***3.10***



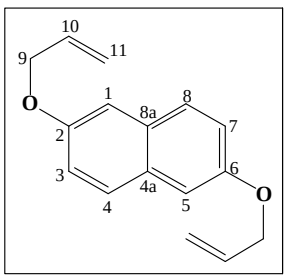
Ligand **3.10** was prepared following the general procedure and was purified by column chromatography. Yield 0.200 g, 33 %. M.p. 60-62 °C ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (2H, d, *J* = 8.2 Hz, H4, H5), 7.34 (2H, t, *J* = 7.9 Hz, H3, H6), 6.87 (2H, d, *J* = 7.7 Hz, H2, H7), 6.19 (2H, dtdd, *J* = 16.9, 5.3, 10.5, 0.9 Hz, H10), 5.60-5.52 (2H, m, H11), 5.34-5.29 (2H, m, H11'), 4.67 (4H, m, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.31, C1, C8; 137.78, C4a; 133.93, C10; 126.53, C3, C6; 121.31, C4, C5; 117.69, C11; 108.46, C2, C7; 70.8, C9. Elem. Anal. found: C, 81.83; H, 7.07. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. ESI-MS: found MH^+ = 241.1217; $C_{16}H_{16}O_2$ requires MH^+ = 241.1229.

2,3-Di(allyloxy)naphthalene, ***3.11***



Ligand **3.11** was prepared following the general procedure and was recrystallised from petroleum ether. Yield 0.510 g, 85 %. M.p. 56–59 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72-7.60 (2H, m, H5, H8), 7.33 (2H, dd, *J* = 6.1, 3.2 Hz, H6, H7), 7.15 (2H, s, H1, H4), 6.17 (2H, ddt, *J* = 17.3, 10.5, 5.3 Hz, H10), 5.50 (2H, ddd, *J* = 17.3, 3.0, 1.4 Hz, H11), 5.33 (2H, ddd, *J* = 10.5, 2.9, 1.4 Hz, H11'), 4.73 (4H, dt, *J* = 5.2, 1.5 Hz, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 149.03, C2, C3; 133.44, C10; 129.55, C4a, C8a; 126.64, C5, C8; 124.52, C6, C7; 118.10, C11; 108.68, C1, C4; 69.85, C9. Elem. Anal. found: C, 79.56; H, 6.76. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. ESI-MS: found M^+ = 240.1148; $C_{16}H_{16}O_2$ requires M^+ = 240.1150.

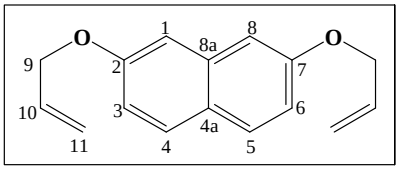
2,6-Di(allyloxy)naphthalene, ***3.12***



2,6-Di(allyloxy)naphthalene was prepared following the general procedure and was recrystallised from pentane to give a crystalline white solid. Yield 0.543 g, 90 %. M.p. 108-110 °C. ^{1}H NMR (300MHz, $CDCl_3$): δ 7.63 (2H, d, *J* = 8.8 Hz, H4, H8), 7.16 (2H, dd, *J* = 8.8, 2.5 Hz, H3, H7), 7.11 (2H, d, *J* = 2.5 Hz, H1, H5), 6.13 (2H, ddt, *J* = 17.3, 10.5, 5.3 Hz, H10), 5.47 (2H,

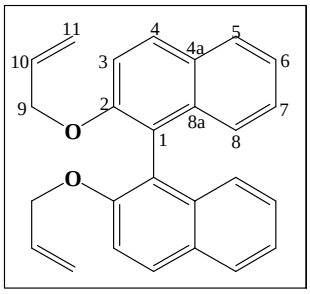
ddd, *J* = 17.3, 3.1, 1.6 Hz, H11), 5.32 (2H, ddd, *J* = 10.6, 2.8, 1.3 Hz, H11'), 4.63 (4H, dt, *J* = 5.3, 1.5 Hz, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 155.41, C2, C6; 133.64, C10; 130.07, C4a, C8a; 128.50, C4, C8; 119.54, C3, C7; 118.00, C11; 107.66, C1, C5; 69.20, C9. Elem. Anal. found: C, 78.85; H, 6.71. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. ESI-MS: found M^+ = 240.1146; $C_{16}H_{16}O_2$ requires M^+ = 240.1150.

2,7-Di(allyloxy)naphthalene, ***3.13***



2,7-Di(allyloxy)naphthalene was prepared following the general procedure and was recrystallised from pentane to give a cream coloured crystalline solid. Yield 0.454 g, 75.7 %. M.p. 63-64 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (2H, d, *J* = 8.5 Hz, H4, H5), 7.05 (4H, s, H1, H3, H6, H8), 6.13 (2H, ddt, *J* = 17.2, 10.5, 5.3 Hz, H10), 5.48 (2H, dq, *J* = 17.2, 1.6 Hz, H11), 5.33 (2H, dq, *J* = 10.5, 1.4 Hz, H11'), 4.65 (2H, dt, *J* = 5.3, 1.5 Hz, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.53, C2, C7; 136.14, C8a; 133.64, C10; 129.56, C4, C5; 124.80, C4a; 118.13, C11; 106.86, C1, C8; 69.17, C9. Elem. Anal. found: C, 79.48; H, 6.75. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. ESI-MS: found M^+ = 240.1156; $C_{16}H_{16}O_2$ requires M^+ = 240.1150.

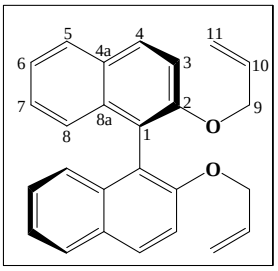
(RS)-2,2'-Di(allyloxy)-1,1'-binaphthalene, ***3.14***



Ligand **3.14** was synthesised from an adapted procedure from the literature.[107] Allyl bromide (0.45 mL, 5 mmol) was added drop-wise over 15 minutes to a mixture of *(RS)*-2,2'-dihydroxy-1,1'-binaphthalene (0.720 g, 2.5 mmol) and potassium carbonate (0.69 g, 5 mmol) in 50 mL acetone. The resulting mixture was refluxed for 5 hrs then filtered and washed with acetone. The filtrate and washings were allowed to cool to room temperature and then a 1 M solution of NaOH was added until **3.14** crystallised out of solution. *(RS)*-2,2'-di(allyloxy)-1,1'-binaphthalene was recrystallised from pentane to give a white crystalline solid. Yield 0.626 g, 68 %. M.p. 89-90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (2H, d, *J* = 9.0 Hz, H4), 7.86 (2H, d, *J* = 8.1 Hz, H8), 7.40 (2H, d, *J* = 9.0 Hz, H3),

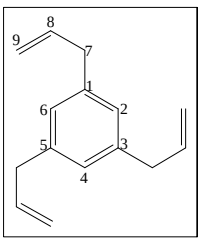
7.32 (2H, t, *J* = 7.3 Hz, H7), 7.26-7.12 (4H, m, H5, H6), 5.84-5.66 (2H, m, H10), 5.08-4.94 (4H, m, H11, H11'), 4.52 (4H, m, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 154.33, C2; 134.43, C8a; 134.05, C10; 129.61, C4a; 129.44, C4; 128.16, C8; 126.51, C6; 125.80, C5; 123.88, C7; 120.68, C1; 116.71, C11; 116.02, C3; 70.27, C9. Elem. Anal. found: C, 84.35; H, 6.08. Calc. for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. ESI-MS: found M^+ = 366.1611; $C_{26}H_{22}O_2$ requires M^+ = 366.1620.

(R)- 2,2'-Di(allyloxy)-1,1'-binaphthalene, ***3.14***



Ligand **3.14** was synthesised from an adapted procedure from the literature.[107] Allyl bromide (0.4 mL, 5 mmol) was added drop-wise over 15 minutes to a mixture of *(R)*-2,2'-di(allyloxy)-1,1'-binaphthalene (286 mg, 1 mmol) and potassium carbonate (276 mg, 2 mmol) in 25 mL acetone. The resulting mixture was refluxed for 5 hrs then filtered and washed with acetone. The filtrate and washings were allowed to cool to room temperature and then a 1 M solution of NaOH was added until **3.14** crystallised out of solution. *(R)*-2,2'-Di(allyloxy)-1,1'-binaphthalene was recrystallised from pentane to give white crystalline needles. M.p. 111-112 °C. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.93 (2H, d, *J* = 9.0 Hz, H4), 7.86 (2H, d, *J* = 8.2 Hz, H8), 7.40 (2H, d, *J* = 9.0 Hz, H3), 7.31 (2H, ddd, *J* = 8.1, 6.6, 1.3 Hz, H7), 7.23-7.18 (2H, m, H6), 7.16-7.13 (2H, m, H5), 5.75 (2H, ddt, *J* = 17.2, 10.6, 4.8 Hz, H10), 5.03-4.97 (4H, m, 1H11, H11'), 4.52 (4H, dt, *J* = 4.8, 1.7 Hz, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 154.30, C2; 134.40, C8a; 134.03, C10; 129.59, C4a; 129.41, C4; 128.12, C8; 126.48, C6; 125.77, C5; 123.85, C7; 120.66, C1; 116.69, C11; 116.00, C3; 70.27, C9. Elem. Anal. found: C, 84.32; H, 6.12. Calc. for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. ESI-MS: found MH^+ = 367.1691; $C_{26}H_{22}O_2$ requires MH^+ = 367.1698.

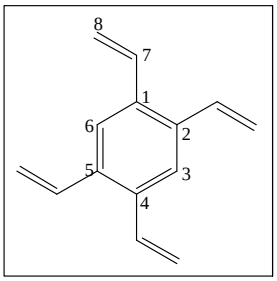
1,3,5-Triallylbenzene, ***4.8***



A solution of 1,3,5-tribromobenzene (0.315 g, 1.5 mmol), LiCl (25 mg, 0.6 mmol), tetrakis-(triphenylphosphine)palladium(0) (69 mg, 6 mol-%) and allyltributylstannane (1 mL, 3.3 mmol) in 10 mL anhydrous dioxane was gently refluxed under argon for 40 hours. After the

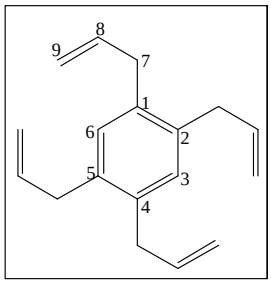
reaction mixture cooled to room temperature 75 mL of dichloromethane was added and then extracted with 4×50 mL water. The solvent was then removed *in vacuo* and the residue was run through an alumina plug with petroleum ether. The product was then further purified by chromatography on silica gel with petroleum ether as eluent. The desired product was isolated as a colourless oil. Yield 99.6 mg, 50 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (3H, s, H2, H4, H6), 5.98 (3H, tdd, *J* = 6.8, 16.8, 10.0 Hz, H8), 5.13-5.06 (6H, m, H9, H9'), 3.37 (6H, d, *J* = 6.8 Hz, H7). ^{13}CNMR (300 MHz, $CDCl_3$): δ 140.68, C1, C3, C5; 137.85, C8; 126.89, C2, C4, C6; 115.96, C9; 40.79, C7.

1,2,4,5-Tetravinylbenzene, ***4.10***



The synthesis for **4.10** was adapted from a literature procedure.[189] 1,2,4,5-tetra(bromomethyl)benzene (0.45 g, 1 mmol) was dissolved in acetone along with triphenylphosphine (1.31 g, 5 mmol). The resulting mixture was refluxed for four hours then cooled and the solvent removed. DMSO (35 mL) was added to the residue as well as and 10 mL 37 % aqueous formaldehyde. The mixture was put on ice and 1 g of NaOH in 15 mL water was added drop-wise. The solution was then stirred for four hours. The solution was diluted to 500 mL with water and 1,2,4,5-tetravinylbenzene was extracted with chloroform. It was then purified using column chromatography. Yield 16.4 mg, 9 %. NMR values are consistent with the literature.[190] ^{1}H NMR (300MHz, $CDCl_3$): δ 7.54 (2H, s, H3, H6), 7.00 (4H, q, *J* = 17.13, 6.5 Hz, H7), 5.67 (4H, dd, *J* = 17.4, 1.3 Hz, H8), 5.34 (4H, dd, *J* = 11.0, 1.3 Hz, H8'). ^{13}C NMR (75MHz, $CDCl_3$): δ 135.96, C7; 134.87, C1, C2, C4, C5; 124.58, C3, C6; 116.84, C8.

1,2,4,5-Tetraallylbenzene, ***4.11***

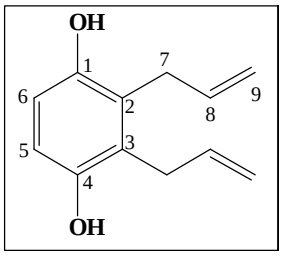


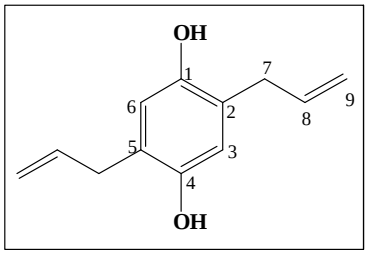
A solution of 1,2,4,5-tetrabromobenzene (0.394 g, 1 mmol), LiCl (33 mg, 0.8 mmol), tetrakis-(triphenylphosphine)palladium(0) (92 mg, 6 mol-%) and allyltributylstannane (1.33 mL, 4.4 mmol) in 10 mL anhydrous dioxane was heated at 100 °C under argon for 72 hours. After the reaction mixture cooled to room temperature

75 mL of dichloromethane was added and then extracted with 4×50 mL water. The solvent was then removed *in vacuo* and the residue was washed through an alumina plug with petroleum ether. The product was then purified by chromatography on alumina with petroleum ether as the eluent. The title compound was isolated as a colourless oil. Yield 102.6 mg, 43 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.98 (2H, s, H3, H6), 6.04-5.91 (4H, m, H8), 5.07 (4H, dd, *J* = 10.1, 1.4 Hz, H9'), 5.06-5.00 (4H, m, H9), 3.38 (8H, m, H7). ^{13}CNMR (300 MHz, $CDCl_3$): δ 137.70, C8; 136.36, C1, C2, C4, C5; 131.24, C3, C6; 115.91, C9; 37.15, C7. Elem. Anal. found: C, 90.78; H, 9.42. Calc. for $C_{18}H_{22}$: C, 90.70; H, 9.30.

1,4-Diallyl-3,6-dihydroxybenzene and 1,2-diallyl-3,6-dihydroxybenzene

Compound **2.9** (3.81 g, 0.2 mol) was place in a round bottom flask with a stirrer and was fitted with a reflux condenser. It was then heated, neat, to 180 °C under argon for 24 hours. Sublimate of both the 1,4- and 1,2-diallyl isomers (0.433 g) was collected from the reflux condenser and the residue is treated with 40 mL of 5M NaOH and washed with 2×25 mL petroleum ether. It is then acidified with 5M HCl and the remaining product was extracted with 3×25 mL diethyl ether. Total yield of both isomers is 2.81 g, 74 %. Isomers are separated with difficulty with column chromatography with 40:100 ethyl acetate:petroleum ether. ^{1}H NMR

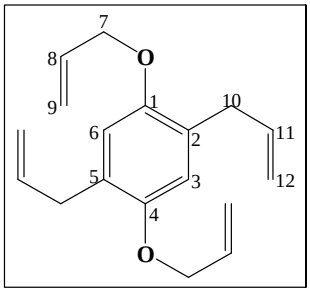




1,4-Diallyl-3,6-dihydroxybenzene ^{1}H NMR (300 MHz, $CDCl_3$): 6.63 (2H, s, H3, H6), 6.04-5.88 (2H, m, H8), 5.10-4.94 (4H, m, H9, H9'), 3.41 (4H, dt, *J* = 5.7, 1.8 Hz, H7).

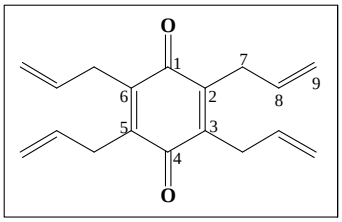
1,2-Diallyl-3,6-dihydroxybenzene ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.59 (2H, s, H5, H6), 6.03-5.89 (2H, m, H8), 5.20-5.11 (4H, m, H9, H9'), 3.33 (4H, m, H7).

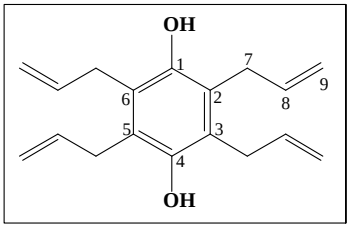
1,4-Diallyl-3,6-di(allyloxy)benzene, ***4.12***



1,4-diallyl-3,6-dihydroxybenzene (0.200 g, 1 mmol) was dissolved in 30 mL acetone. Potassium carbonate (276 mg, 2 mmol) and allylbromide (0.17 mL, 2 mmol) were added to the stirred solution. The resulting mixture was then refluxed overnight. The solution was filtered and the solvent removed *in vacuo*. A solution of 1 M NaOH (20 mL) was added to the residue and the desired product was extracted with pentane. No further purification was necessary. Yield 86 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.69 (2H, s, H3, H6), 6.09-5.93 (4H, m, H8, H11), 5.41 (2H, ddd, *J* = 17.2, 3.2, 1.5 Hz, H9), 5.25 (2H, dd, *J* = 10.5, 1.5 Hz, H9'), 5.11-5.01 (4H, m, H12,H12'), 4.49 (4H, dt, *J* = 5.1, 1.4 Hz, H7), 3.39 (4H, d, *J* = 6.7 Hz, H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 150.63, C1, C4; 137.37, C8; 134.15, C11; 127.77, C3, C6; 117.08, C9; 115.74, C2, C5; 114.81, C12; 70.10, C7; 34.57, C10. Elem. Anal. found: C, 77.66; H, 8.20. Calc. for $C_{18}H_{22}O_2.½H_2O$: C, 77.38; H, 8.30. ESI-MS: found MH^+ = 271.1771; $C_{18}H_{22}O_2$ requires MH^+ = 271.1698.

2,3,5,6-Tetraallylbenzoquinone, ***4.13*** *and 2,3,5,6-tetraallylhydroquinone*



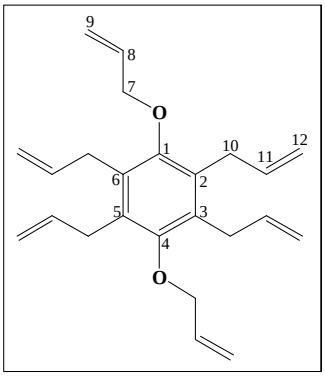


An isomeric mix of 1,4-diallyl-3,6-di(allyloxy)benzene and 1,2-diallyl-3,6-di(allyloxy)benzene (1.003 g, 5.3 mmol) was place in a round bottom flask and heated to 180 °C under argon with constant stirring. After heating the residue is treated with 40 mL of 5M NaOH and washed with 2×25 mL petroleum ether, then acidified with 5M HCl and the product was extracted with 3×25 mL diethyl ether. Ligand **4.13** and 2,3,5,6-tetraallyl-1,4-dihydroxyhydroquinone were separated by column chromatography. Conversion of the hydroquinone to the benzoquinone occurs upon standing.

2,3,5,6-Tetraallyl-hydroquinone: Yield 0.361 g, 36 % . ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.02-5.89 (4H, m, H8), 4.99 (4H, ddd, *J* = 10.3, 3.6, 1.8 Hz, H9,), 4.90-4.83 (4H, m, H9'), 3.43 (8H, dt, *J* = 5.4, 1.88 Hz, H7).

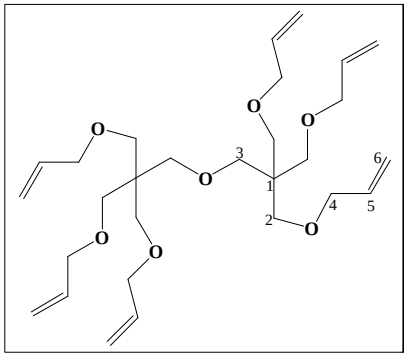
2,3,5,6-Tetraallylquinone: Yield 0.426 g, 42 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.83 (4H, tdd, J = 6.3, 16.5, 10.2 Hz, H8), 5.20-4.98 (8H, m, H9, H9'), 3.31 (8H, d, J = 6.3 Hz, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 186.90, C1, C4; 142.52, C2, C3, C5, C6; 134.14, C8; 116.99, C9; 30.74, C7. Elem. Anal. found: C, 77.57; H, 7.38. Calc. for $C_{18}H_{20}O_2.H_2O$: C, 77.95; H, 7.63. ESI-MS: found MH^+ = 269.1542; $C_{18}H_{20}O_2$ requires MH^+ = 269.1542.

1,2,4,5-Tetraallyl-3,6-di(allyloxy)benzene, ***4.14***



2,3,5,6-Tetraallylquinone (318 mg, 1.37 mmol), allyl bromide (1.25 mL, 0.014 mol) and potassium carbonate (1.79 g, 0.013 mol) were added to 30 mL dry THF. Portions of sodium borohydride were added to the stirred mixture until it went colourless. It was then heated under argon to 65 °C and portions of sodium borohydride were added periodically until a total of 400 mg had been added over 24 hours. Water (100 mL) was then slowly added and the product is extracted with diethyl ether. The crude product was then treated to the same process again. Yield 8.1 mg, 2 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.15-5.87 (6H, m, H8, H11), 5.42 (2H, dd, *J* = 17.2, 1.7 Hz, H9), 5.23 (2H, dd, *J* = 10.5, 1.4 Hz, H9'), 5.00 (4H, dd, *J* = 10.2, 1.8 Hz, H12'), 4.88 (4H, dd, *J* = 17.2, 1.8 Hz, H12), 4.27 (4H, td, *J* = 1.2, 5.1 Hz, H7), 3.44 (8H, td, *J* = 1.7, 5.3 Hz, H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 153.05, C1, C4; 137.84, C11; 134.49, C8; 131.43, C2, C3, C5, C6; 116.85, C9; 115.19, C12; 75.23, C7; 31.25, C10; 30.1. MH^+ = 351.2339; $C_{24}H_{30}O_2$ requires MH^+ = 351.2324.

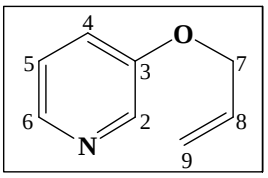
Hexa-O-allyl-dipentaerythritol, ***5.7***



Ligand **5.7** was prepared using an adapted literature procedure.[167] Dipentaerythritol (1.87 g, 7.35 mmol) and tetrabutylammonium fluoride (0.9 g) was dissolved in 40 mL 33 % aqueous NaOH. Allyl bromide (5 mL) was added drop-wise and the resulting solution was stirred vigorously at 70 °C for 72 hrs. The product was extracted with toluene (2 × 40 mL) and purified by

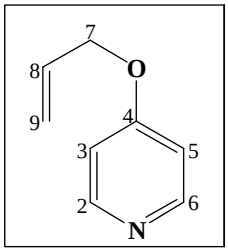
column chromatography. Yield 1.310 g, 36 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.86 (6H, tdd, *J* = 5.4, 17.2, 10.6 Hz, H5), 5.23 (6H, ddd, *J* = 17.3, 3.5, 1.7 Hz, H6), 5.11 (6H, ddd, *J* = 10.4, 3.1, 1.4 Hz, H6'), 3.92 (12H, td, *J* = 1.5, 5.3 Hz, H4), 3.42 (12H, s, H2), 3.38 (4H, s, H3). ^{13}C NMR (75MHz, $CDCl_3$): δ 135.68, C5; 116.46, C6; 72.68, C4; 70.49, C3; 69.83, C2; 45.98, C1. Elem. Anal. found: C, 66.71; H, 9.62. Calc. for $C_{28}H_{46}O_7.½H_2O$: C, 66.77; H, 9.41. ESI-MS: found MH^+ = 495.3315; $C_{28}H_{46}O_7$ requires MH^+ = 495.3322.

3-Allyloxypyridine, ***6.11***



3-Hydroxypyridine (1.9 g, 0.02 mol), potassium carbonate (2.76 g, 0.02 mol) and allylbromide (1.8 mL, 0.02 mol) were refluxed together in acetone (50 mL) for 5 hours. The mixture was then filtered and the filtrate was collected and the solvent was removed *in vacuo*. To the residue, 60 mL of 1M NaOH was added and the desired product was extracted with diethyl ether and run through a short silica plug. 3-Allyloxypyridine was isolated as a brownish red oil. Yield 0.162 g, 6 %. Proton NMR is comparable to literature values.[191] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (1H, s, H2), 8.25 (1H t, *J* = 2.8 Hz, H5), 7.29-7.20 (2H, m, H4, H6), 6.17-5.99 (1H, m, H8), 5.53-5.41 (1H, m, H9), 5.40-5.28 (1H, m, H9'), 4.62 (2H, m, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 154.73, C3; 142.03, C6; 138.00, C2; 132.42, C8 123.82, C5; 121.52, C4; 118.26, C9; 69.00, C7.

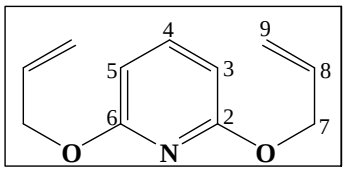
4-Allyloxypyridine, ***6.12***



Sodium (1.04 g, 45.2 mmol) was added to allyl alcohol (10 mL) and stirred under argon for 1 hour. 4-bromopyridine hydrochloride (2.2 mL, 23.1 mmol) was added and the reaction mixture was heated to 115 °C for 20 hours. The mixture was then allowed to cool and water (30 mL) was added. The product was then extracted with diethyl ether, dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by chromatography gave 4-allyloxypyridine as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (2H, d, *J* = 5.3 Hz, H2, H6), 6.92-6.78 (2H, m, H3, H5), 6.18-5.94 (1H, m, H8), 5.44 (1H, dd, *J* = 17.2, 1.2 Hz, H9), 5.35 (1H, dd, *J* = 10.5, 1.1 Hz, H9'), 4.60 (2H, dd, *J*

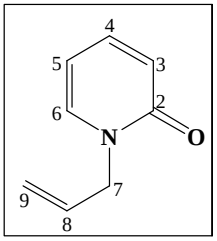
= 5.3, 1.1 Hz, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 164.64, C4; 150.63, C2, C6; 131.79, C8; 118.47, C9; 110.46, C3, C5; 68.44, C7.

2,6-Di(allyloxy)pyridine, ***6.13***



Sodium (1.04 g, 45.2 mmol) was added to allyl alcohol (10 mL) and stirred under argon for 1 hour. 2,6-Dibromopyridine (2.672 g, 11.3 mmol) was added and the reaction mixture was heated to 115 °C for 20 hours. The mixture was then allowed to cool and water (30 mL) was added. The product was then extracted with diethyl ether, dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography; silica gel with 1:10 diethyl ether:petroleum ether. Yield 2.002 g, 93 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (1H, t, *J* = 7.9 Hz, H4), 6.32 (2H, d, *J* = 7.9 Hz, H3, H5), 6.09 (2H, tdd, *J* = 5.6, 17.2, 10.5 Hz, H8), 5.39 (2H, dd, *J* = 17.3, 1.6 Hz, H9), 5.25 (2H, ddd, *J* = 10.4, 2.7, 1.3 Hz, H9'), 4.80 (4H, td, *J* = 1.4, 5.6 Hz, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 162.05, C2, C6; 140.94, C4; 133.61, C8; 117.36, C9; 101.53, C3, C5; 66.49, C7. ESI-MS: found MH^+ = 192.1015; $C_{11}H_{13}NO_2$ requires MH^+ = 192.1025.

1-Allyl-2-pyridone, ***6.14***

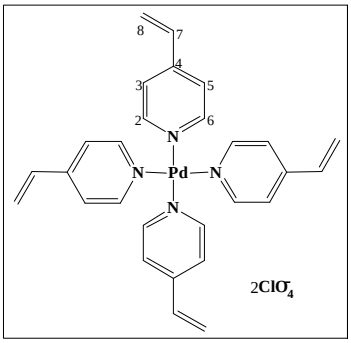


2-Hydroxypyridine (2 g, 0.021 mol), potassium carbonate (2.9 g, 0.021 mol) and allylbromide (1.85 mL, 0.021 mol) were refluxed together in acetone (50 mL) for 5 hours. The mixture was then filtered and the filtrate was collected and the solvent was removed *in vacuo*. To the residue, 60 mL of 1M NaOH was added and the desired product was extracted with petroleum ether. Yield 1.298 g, 46 %. NMR is consistent with literature values.[192] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (1H, ddd, *J* = 8.8, 6.7, 2.1 Hz, H4), 7.23 (1H, dd, *J* = 6.8, 2.0 Hz, H6), 6.56 (1H, d, *J* = 9.2 Hz, H3), 6.16 (1H, dt, *J* = 6.7, 1.3 Hz, H5), 5.93 (1H, tdd, *J* = 5.8, 17.1, 10.3 Hz, H8), 5.28-5.20 (1H, m, H9), 5.18-5.11 (1H, m, H9'), 4.54 (1H, td, *J* = 1.4, 5.7 Hz, H7). ^{13}C NMR (75MHz, $CDCl_3$): δ 162.08, C2; 139.24, C4; 136.83, C6; 132.11, C8; 120.60, C3 118.02, C9; 105.87, C5; 50.63, C7.

Dichloro-bis-(4-vinylpyridine) palladium, ***6.28***

Dichlorobisbenzonitrile palladium (0.260 g, 0.68 mmol) was dissolved in 5 mL chloroform and a solution of 4-vinylpyridine (0.14 g, 1.36 mmol) in 5 mL chloroform was added. The resulting solution was left to stir overnight when a yellow precipitate slowly forms. The mixture was then filtered yielding dichloro-bis-(4-vinylpyridine) palladium. Yield 0.230 g, 87 %. Decomp. 230 – 260 °C. Elem. Anal. found: C, 43.61; H, 3.67; N, 7.16. Calc. for $C_{14}H_{14}N_2Cl_2Pd$: C, 43.38; H, 3.64; N, 7.23 ESI-MS: found MH^+ = 386.9641; $C_{14}H_{14}N_2Cl_2Pd$ requires MH^+ = 386.9647.

Tetrakis(4-vinylpyridine) palladium (II) perchlorate, ***6.29***



Dichlorobis4vinylpyridine palladium (78 mg, 0.2 mmol) was added to a solution of silver(I) perchlorate (84.1 mg, 0.4 mmol) in 10 mL of acetone. The resulting mixture was left for 3 days then filtered. The filtrate was collected and the solvent removed *in vacuo*. A solution of 4-vinylpyridine (64.2 mg, 0.6 mmol) in 7 mL chloroform is added to the residue and diethyl ether was allowed to slowly diffuse into the solution. Yield 58.9 mg, 41 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.16 (2H, d, *J* = 4.9 Hz, H2, H6), 7.38 (2H, d, *J* = 4.8 Hz, H3, H5), 6.57 (1H, dd, *J* = 17.3, 10.8 Hz, H7), 6.00 (1H, d, *J* = 17.5 Hz, H8), 5.62 (1H, d, *J* = 10.6 Hz, H8'). ^{13}C NMR (75MHz, $CDCl_3$): δ 151.80, C2, C6; 148.95, C4; 132.92, C7; 124.12, C3, C5; 123.85, C8. Elem. Anal. found: C, 45.60; H, 4.29; N, 6.68. Calc. for $C_{28}H_{28}N_4O_8Cl_2Pd.H_2O$: C, 45.21; H, 4.06; N, 7.53.

8.3 Complex Preparation

Complexes of **1.28**

<u>With silver(I) perchlorate viz **2.10**</u>

1,4-Divinylbenzene (13 mg, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (20.5 mg, 0.1 mmol) also dissolved in 1 ml acetone. The mixture was left in darkness at room temperature and the solvent was allowed to evaporate. This

enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Elem. Anal. found: C, 33.11; H, 2.99. Calc for $C_{10}H_{10}AgClO_4.H_2O$: C: 33.78; H: 3.40.

Complexes of **2.6**

With silver(I) perchlorate viz **2.11**

1,4-Diallylbenzene (16 mg, 0.1 mmol) was dissolved in 4 ml toluene and was combined with silver(I) perchlorate (20.5 mg, 0.1 mmol) dissolved in 4 ml toluene. The solution was kept in darkness and was subjected to vapour diffusion of petroleum ether. Colourless crystals precipitated out of solution over a 24 hour period and were suitable for single crystal X-ray analysis.

With silver(I) trifluoroacetate viz **2.12**

1,4-Diallylbenzene (16 mg, 0.1 mmol) was dissolved in 4 ml chloroform and was added to silver(I) perchlorate (20.5 mg, 0.1 mmol) dissolved in 4 ml acetone. The solution was kept in darkness and was subjected to vapour diffusion of diethyl ether. Colourless crystals, suitable for single crystal X-ray analysis, formed after the evaporation of all the solvents.

Complexes of **2.9**

With silver(I) perchlorate viz **2.13**

1,4-Di(allyloxy)benzene (19 mg, 0.1 mmol) was dissolved in 4 ml chloroform and was added to silver(I) perchlorate (20.5 mg, 0.1 mmol) dissolved in 4 ml acetone. The solution was kept in darkness at 5°C and the solvent was allowed to evaporate. This enabled the formation of colourless crystals suitable for single crystal X-ray analysis. Yield 29.3 mg, 64 %. M.p. 106 °C. Elem. Anal. found: C, 38.92; H, 4.35. Calc for $5C_{12}H_{14}O_2AgClO_4.4CH_3COCH_3$: C, 38.95; H, 4.27.

With silver(I) tetrafluoroborate viz **2.14**

1,4-Di(allyloxy)benzene (19 mg, 0.1 mmol) was dissolved in 8 mL chloroform and was added to solid silver(I) tetrafluoroborate (19.5 mg, 0.1 mmol). The mixture was left in darkness at room temperature for 48 hours and then the solvent was allowed to evaporate.

After evaporation of the solvent colourless crystals suitable for single crystal X-ray analysis were left behind. Yield 3.6 mg, 9 %. Elem. Anal. found: C, 38.47; H, 4.46. Calc for $C_{24}H_{28}O_4Ag_2B_2F_8.H_2O.CH_3COCH_3$: C, 38.34; H, 4.29.

Complex of **2.8**

With silver(I) hexafluorosilicate viz **2.15**

1,3-Di(allyloxy)benzene (19. mg, 0.1 mmol) was dissolved in 8 mL toluene and added to silver(I) hexafluorophosphate (20 mg, 0.1 mmol). The solution was kept in darkness at room temperature where the toluene was allowed to slowly evaporate. Slow decomposition of hexafluorophosphate yielded a few crystals of **2.15**. Insufficient sample to carry out further characterisation.

Complexes of **2.7**

With silver(I) perchlorate viz **2.16**

1,2-Di(allyoxybenzene (19 mg, 0.1 mmol) was dissolved in 4 mL chloroform and was added to a solution of silver(I) perchlorate (20.5 mg, 0.1 mmol) in 4 mL acetone. The solution was kept in darkness at 5 °C and ether was allowed to diffuse in over time. All solvents were then allowed to evaporate enabling the formation of colourless crystals suitable for single crystal X-ray analysis. M.p. 55°C.

With silver(I) hexafluorophosphate viz **2.17**

1,2 Di(allyloxy)benzene (19 mg, 0.1 mmol) was dissolved in 4 mL chloroform and was added to a solution of silver(I) hexafluorophosphate (25 mg, 0.1 mmol) in 4 mL acetone. The solution was kept in darkness at 5 °C and ether was allowed to diffuse in over time. All solvents were then allowed to evaporate enabling the formation of colourless crystals suitable for single crystal X-ray analysis. M.p. 90-91°.

With silver(I) triflate viz **2.18**

1,2-Di(allyoxybenzene (19 mg, 0.1 mmol) was dissolved in 4 mL chloroform and was added to a solution of silver(I) triflate (25.5 mg, 0.1 mmol) in 4 mL acetone. The solution was kept in darkness at 5 °C and ether was allowed to diffuse in over time. All solvents

were then allowed to evaporate enabling the formation of colourless crystals suitable for single crystal X-ray analysis. Yield 19.3 mg, 43 %. M.p. 83-84°C. Elem. Anal. found: C, 34.74; H, 3.24. Calc. for $C_{13}H_{14}O_2AgCF_3SO_3$: C, 34.92; H, 3.16.

Complex of **3.8**

With silver(I) perchlorate viz **3.16**

1,4-Di(allyloxy)naphthalene (12 mg, 0.05 mmol) dissolved in 4 mL chloroform was added to silver(I) perchlorate (10 mg, 0.05 mmol) dissolved in 4 mL acetone. The solution was left in darkness at 5 °C and diethyl ether was allowed to diffuse in. After 7 days all solvent was then allowed to evaporate. This enabled the formation of colourless crystals suitable for single crystal X-ray analysis. Yield 13.1 mg, 59 %. Decomp. 90 °C.

Complexes of **3.9**

With silver(I) triflate viz **3.17**

1,5-Di(allyloxy)naphthalene (24 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) triflate (25.5 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to diffuse in. After 14 days all solvent was then allowed to evaporate. This enabled the formation of colourless crystals suitable for single crystal X-ray analysis. Yield 10.5 mg, 28 %. Decomp. 121°C. Elem. Anal. found: C, 28.81; H, 2.94. Calc for $C_8H_8OAgCF_3SO_3$: C, 28.67; H, 2.14.

Complex of **3.10**

With silver(I) triflate viz **3.18**

1,8-Di(allyloxy)naphthalene (24 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) triflate (25.5 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to diffuse in. The solvents were then allowed to slowly evaporate yielding crystals suitable for single crystal X-ray analysis. Yield 18.1 mg, 36 %. Decomp. 104 °C. Elem. Anal. found: C, 41.33; H, 3.31. Calc for $C_{16}H_{16}O_2AgCF_3SO_3$: C, 41.06; H, 3.24.

With silver(I) perchlorate viz **3.19**

1,8-Di(allyloxy)naphthalene (24 mg, 0.1 mmol) was dissolved in 4 ml chloroform and added to silver(I) perchlorate (20.5 mg, 0.1 mmol) dissolved in 4 ml acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to diffuse in. The solvents were then allowed to slowly evaporate yielding crystal suitable for single crystal X-ray analysis. Yield 13.9 mg, 30 %. Elem. Anal. found: C, 43.79; H, 4.06. Calc for $C_{16}H_{16}O_2AgClO_4.½CH_3COCH_3$: C, 44.10; H, 4.02.

Complex of **3.11**

With silver(I) hexafluorophosphate viz **3.20**

2,3-Di(allyloxy)naphthalene (24 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) hexafluorophosphate (25 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to diffuse in. After 14 days all solvent was then allowed to evaporate. This enabled the formation of colourless crystals suitable for single crystal X-ray analysis. Yield 14.7 mg, 30 %. M.p. 140 - 146°C. Elem. Anal. found: C, 39.24; H, 3.40. Calc for $C_{16}H_{16}O_2AgPF_6$: C, 38.97; H, 3.27.

Complex of **3.12**

With silver(I) tetrafluorobrate viz **3.21**

2,6-Di(allyloxy)naphthalene (24 mg, 0.1 mmol) was dissolved in 8 mL chloroform and added to solid silver(I) tetrafluoroborate (19.5 mg, 0.1 mmol). The mixture was left in darkness at room temperature for 48 hours and then the solvent was allowed to evaporate. After evaporation of the solvent colourless crystals suitable for single crystal X-ray analysis were left behind. Yield 2.7 mg, 6 %.

Complex of **3.13**

With silver(I) triflate viz **3.22**

2,7-Di(allyloxy)naphthalene (24 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) triflate (25.5 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to diffuse in. After 14 days all solvent was then allowed to evaporate. This enabled the formation of colourless

crystals suitable for single crystal X-ray analysis. Yield 9.6 mg, 19 %. M.p. 107 - 110°C. Elem. Anal. found: C, 40.18; H, 3.93. Calc for $C_{16}H_{16}O_2AgCF_3SO_3.½H_2O$: C, 40.33; H, 3.38.

Complexes of **3.14**

With silver(I) perchlorate viz **3.23** and **3.24**

2,2'-Di(allyloxy)-binaphthalene (36.5 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) perchlorate (20.5 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at 5°C and diethyl ether was allowed to diffuse in. After 7 days all solvent was then allowed to evaporate. This enabled the formation of colourless crystals suitable for single crystal X-ray analysis. M.p. 51-54°C.

(R)-2,2'-Di(allyloxy)-binaphthalene (36.5 mg, 0.1 mmol) was dissolved in 4 ml chloroform and was added to silver(I) perchlorate (41 mg, 0.2 mmol) dissolved in 4 ml acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to diffuse in. The solvents were then allowed to slowly evaporate yielding crystal suitable for single crystal X-ray analysis.

Complex of **4.7**

With silver(I) perchlorate viz **4.17**

1,3,5-Trivinylbenzene (15.5 mg, 0.1 mmol) was dissolved in 4 ml chloroform and added to silver(I) perchlorate (20.5 mg, 0.1 mmol) dissolved in 4 ml acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to diffuse in. The solvents were then allowed to slowly evaporate yielding crystal suitable for single crystal X-ray analysis. Yield 27.8 mg, 58 %.

Complexes of **4.10**

With silver(I) perchlorate viz **4.18**

1,2,4,5-Tetravinylbenzene (18.0 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) perchlorate (41.4mg, 0.2 mmol) dissolved in 4 mL acetone. The mixture was left in darkness at 5 °C and diethyl ether was allowed to diffuse in. Within 5 hours

crystals suitable for single crystal X-ray analysis had precipitated. Yield 9.4 mg, 25 %. Decomp. >129 °C.

With silver(I) perchlorate viz **4.19**

1,2,4,5-Tetravinylbenzene (9 mg, 0.05 mmol) was dissolved in 4 ml chloroform was added to silver(I) perchlorate (20.5 mg, 0.1 mmol) also dissolved in 4 ml acetone. The mixture was left in darkness at room temperature and the solvent was allowed to slowly evaporate giving colourless crystals.

With silver(I) tetrafluoroborate viz **4.20**

1,2,4,5-Tetravinylbenzene (9 mg, 0.05 mmol) was dissolved in 8 mL and added to solid silver(I) tetrafluoroborate (39 mg, 0.2 mmol). The mixture was left in darkness at room temperature for 48 hours and then the solvent was allowed to evaporate. After evaporation of the solvent colourless crystals suitable for single crystal X-ray analysis were left behind.

Complexes of **4.11**

With silver(I) triflate viz **4.21**

1,2,4,5-Tetraallylbenzene (12 mg, 0.05 mmol) in 1 mL toluene was added to a 4 mL solution of silver(I) triflate (25.5 mg, 0.1 mmol) in toluene. Upon addition of the ligand a white solid precipitated out and was filtered off. The filtrate was kept in darkness at room temperature and petroleum ether was allowed to vapour diffuse in. This process yielded colourless crystals suitable for single crystal X-ray diffraction which formed overnight.

Complexes of **4.13**

With silver(I) hexafluorophosphate viz **4.22**

2,3,4,5-Tetraallylbenzonquinone (27 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) hexafluorophosphate (50.5 mg, 0.2 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to vapour diffuse into the solution. Yellow crystals suitable for single crystal X-ray analysis precipitate out of solution after 72 hrs. Yield 29 mg, 35 %.

With silver(I) triflate viz **4.23**

2,3,4,5-Tetraallylbenzoquinone (27 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) triflate (51.5 mg, 0.2 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to diffuse into the solution. Yellow crystals suitable for single crystal X-ray analysis formed after solvent evaporation. Yield 38.7 mg, 50 %. Decomp. >125 °C. Elem. Anal. found: C, 30.91; H, 2.74. Calc for $C_9H_{10}OAgCF_3SO_3$: C, 30.71; H, 2.58.

Complexes of **4.12**

With silver(I) perchlorate viz **4.24**

1,4-Di(allyloxy)-2,5-diallylbenzene (27 mg, 0.1 mmol) was dissolved in 4 ml chloroform and added to silver(I) perchlorate (41 mg, 0.2 mmol) dissolved in 4 ml acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to diffuse in. Upon evaporation of solvent crystals suitable for single crystal X-ray diffraction were formed. Yield 29.7 mg, 37 %. Explosive decomposition at 119 °C. Elem. Anal. found: C, 32.41; H, 3.62. Calc for $C_9H_{11}OAgClO_4.{}^1/_6CH_3COCH_3$: C: 32.40; H: 3.43.

With silver(I) hexafluorophosphate viz **4.25**

1,4-Di(allyloxy)-2,5-diallylbenzene (27 mg, 0.1 mmol) was dissolved in 4 ml chloroform and added to silver(I) hexafluorophosphate (25 mg, 0.1 mmol) also dissolved in 4 ml acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to diffuse in. Evaporation of the solvents yielded yellow crystals suitable for single crystal X-ray analysis. Yield 25.5 mg, 57 %. Decomp 105 °C. Elem. Anal. found: C, 33.11; H, 4.20. Calc for $C_9H_{11}OAgPF_6.1½CH_3COCH_3.½H_2O$: C: 33.49; H: 4.37.

Complex of **5.1**

With silver(I) triflate viz **5.10**

Diallylether (10 mg, 0.1 mmol) dissolved in 4 mL chloroform and was added to silver(I) triflate (25.5 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to vapor diffuse into the solution.

Colourless crystals suitable for single crystal X-ray analysis formed after solvent evaporation. Yield 12.5 mg, 19 %. Decomp. 104 °C. Elem. Anal. found: C, 16.24; H, 1.95. Calc for $C_6H_{10}OAg_2C_2F_6S_2O_6.3H_2O$: C, 14.43; H, 2.42.

Complexes of **5.4**

With silver(I) perchlorate viz **5.11**

Triallylamine (13.5 mg, 0.1 mmol) was dissolved in 4 ml chloroform and was added to silver(I) perchlorate (20.5 mg, 0.1 mmol) dissolved in 4 ml acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to vapor diffuse in. Crystals suitable for single crystal X-ray analysis precipitated from solution. The evaporation of all solvents yielded further crystalline product. Yield 10.8 mg, 31 %. Decomp. 117 °C. Elem. Anal. found: C, 31.40; H, 4.63; N, 3.96. Calc for $C_9H_{15}NAgClO_4$: C, 31.37; H, 4.39; N, 4.07.

With silver(I) hexafluorophosphate viz **5.12**

Triallylamine (13.5 mg, 0.1 mmol) was dissolved in 4 ml chloroform and added to silver(I) hexafluorophosphate (25 mg, 0.1 mmol) also dissolved in 4 ml acetone. The solution was left in darkness at room temperature and ether was allowed to diffuse in. Colourless crystals suitable for single crystal X-ray diffraction precipitated from the solution. Yield 15.8 mg, 40.5 %. Decomp. 137 °C. Elem. Anal. found: C, 27.92; H, 3.98; N, 3.58. Calc for $C_9H_{15}NAgPF_6$: C, 27.71; H, 3.88; N, 3.59.

With silver(I) triflate viz **5.13**

Triallylamine (13.5 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) triflate (25.5 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to diffuse in. The solvents were then allowed to evaporate yielding crystals suitable for single crystal X-ray analysis. Yield 18.2 mg, 46 %. Decomp 118 °C. Elem. Anal. found: C, 30.55; H, 3.96; N, 3.46. Calc for $C_9H_{15}NAgCF_3SO_3$: C, 30.47; H, 3.84; N, 3.55.

With silver(I) nitrate viz **5.14**

Triallylamine (13.5 mg, 0.1 mmol) dissolved in 8 mL acetone was added to 0.1 mmol of silver(I) nitrate. The mixture was stored in darkness at room temperature while the solvent was allowed to slowly evaporate. Completion of evaporation furnished crystalline residue suitable for single crystal X-ray structure analysis. Yield 14.4 mg, 47 %. M.p. 56 -58 °C.

Complex of **5.6**

With silver(I) perchlorate viz **5.15**

Tetra-O-allyl-pentaerythritol (28 mg, 0.1 mmol) was dissolved in 4 ml chloroform and added to silver(I) perchlorate (41 mg, 0.2 mmol) also dissolved in 4 ml acetone. The mixture was left in darkness at room temperature and the solvent was allowed to evaporate yielding colourless crystals. Yield 22.3 mg, 33 %. Decomp. 142 °C.

Complexes with **6.10**

With silver(I) perchlorate viz **6.16**

2-Allyloxypyridine (13.5 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) perchlorate (103.5 mg, 0.5mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to vapor diffuse into the solution. Colourless crystals suitable for single crystal X-ray analysis formed rapidly from the solution. Yield 13.7 mg, 40 %. Decomp. 119 °C. Elem. Anal. found: C, 27.92; H, 2.84; N, 4.05. Calc for $C_8H_9NOAgClO_4$: C, 28.06; H, 2.65; N, 4.09.

With silver(I) triflate viz **6.17**

2-Allyloxypyridine (13.5 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) triflate (127.5 mg, 0.5 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to vapour diffuse into the solution. Crystals suitable for single crystal X-ray analysis formed after solvent evaporation. Yield 33.9 mg, 86 %. M.p. 139 – 142 °C.

Complexes of **6.11**

With silver(I) perchlorate viz **6.18**

3-Allyloxypyridine (13.5 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) perchlorate (103.5 mg, 0.5mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to vapor diffuse into the solution. Colourless crystals suitable for single crystal X-ray analysis formed rapidly from the solution. Yield 14.1 mg, 42 %. Decomp. 109 °C. Elem. Anal. found: C, 27.13; H, 2.68; N, 3.49. Calc for $C_8H_9NOAgClO_4.½H_2O$: C, 27.34; H, 2.87; N, 3.98

With copper(I) iodide viz **6.19**

3-Allyloxypyridine (135 mg, 1 mmol) dissolved in 4 mL methanol was added to a stirred suspension of copper(I) iodide (190 mg, 1 mmol) in 8 mL methanol. The resulting mixture was stirred for a further 76 hours upon which the solvent was allowed to slowly evaporate. This yielded a few crystals suitable for X-ray analysis. Insufficient sample was isolated for further characterisation.

Complexes of **6.12**

With silver(I) perchlorate viz **6.20**

4-Allyloxypyridine (13.5 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) perchlorate (103.5 mg, 0.5mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to vapor diffuse into the solution. Colourless crystals suitable for single crystal X-ray analysis precipitated from solution over 24 hrs. Yield 10.8 mg, 32 %. Decomp. 111 °C. Elem. Anal. found: C, 27.12; H, 2.74; N, 3.66. Calc for $C_8H_9NOAgClO_4.½H_2O$: C, 27.34; H, 2.87; N, 3.98.

With silver(I) hexafluorophosphate viz **6.21**

4-Allyloxypyridine (13.5 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) hexafluorophosphate (25.5 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to vapor diffuse in. Solvent evaporation yielded crystals suitable for single crystal X-ray analysis. Yield 4 mg, 10 %.

Complexes of **6.13**

With silver(I) perchlorate viz **6.22**

2,6-Diallyloxypyridine (19 mg, 0.1 mmol) dissolved in 4 mL chloroform and was added to silver(I) perchlorate (103.5 mg, 0.5mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to vapour diffuse into the solution. Upon evaporation of solvent colourless crystals formed which were suitable for single crystal X-ray analysis. Yield 18.9 mg, 57 %. Decomp. 108 °C.

With copper(I) chloride viz **6.23**

2,6-Diallylpyridine (37.5 mg, 0.2 mmol) dissolved in 2 mL methanol and added to a solution of copper(II) chloride (34 mg, 0.2mmol) dissolved in 2 mL methanol. A solution of triethylphosphite in methanol (0.3 mmol per mL) was added until the copper solution went colourless. The methanol was reduced to half *in vacuo* and diethyl ether was allowed to diffuse in. A fine white precipitate formed of which a few crystal were suitable for X-ray diffraction. Yield 17.7 mg, 45 %.

Complexes of **6.14**

With silver(I) triflate viz **6.24**

1-Allyl-2-pyridone (13.5 mg, 0.1 mmol) dissolved in 4 mL chloroform was added to silver(I) triflate (25.5 mg, 0.1 mmol) dissolved in 4 mL acetone. The solution was left in darkness at room temperature where diethyl ether was allowed to diffuse in. The solvents were then allowed to slowly evaporate yielding crystals suitable for single crystal X-ray analysis. Yield 10.4 mg, 27 %. M.p. 136-138 °C. Elem. Anal. found: C, 28.39; H, 2.50; N, 3.58. Calc for $C_8H_9ONAgCF_3SO_3$: C, 27.57; H, 2.31; N, 3.57.

With silver(I) hexafluorophosphate viz **6.25**

1-Allyl-2-pyridone (13.5 mg, 0.1 mmol) was dissolved in 4 ml chloroform and added to silver(I) hexafluorophosphate (25 mg, 0.1 mmol) dissolved in 4 ml acetone. The solution was left in darkness at room temperature and the ether was allowed to diffuse in. Upon evaporation of all solvents crystals suitable for single crystal X-ray analysis were formed.

Yield 13.8 mg, 36 %. Decomp. >132 °C. Elem. Anal. found: C, 26.24; H, 2.58; N, 3.65. Calc for $C_8H_9NOAgPF_6.{}^1/_3CH_3COCH_3$: C, 26.54; H, 2.72; N, 3.44.

With silver(I) perchlorate viz **6.26**

1-Allyl-2-pyridone (13.5 mg, 0.1 mmol) was dissolved in 4 ml chloroform and added to silver(I) perchlorate (20.5 mg, 0.1 mmol) dissolved in 4 ml acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to vapor diffuse in. Crystals suitable for single crystal X-ray analysis precipitated from the solution. Evaporation of the solvents yielded further crystalline product. Yield 10.8 mg, 32 %. Decomp. 175 °C. Elem. Anal. found: C, 28.91; H, 2.86; N, 4.04. Calc for $C_8H_9NOAgClO_4$: C, 28.06; H, 2.65; N, 4.09.

Complex of **6.2**

With silver(I) nitrate viz **6.27**

4-Vinylpyridine (10.5 mg, 0.1 mmol) was dissolved in 2 mL dichloromethane and mixed with cobalt(II) nitrate (36.5 mg, 0.2 mmol) dissolved in acetone and left for one week. Silver(I) perchlorate (41.5 mg, 0.2 mmol) dissolved in acetone was then added and the solution was kept in darkness while allowing the solvents to evaporate. This enabled the formation of crystals that were suitable for single crystal X-ray diffraction. Yield 32.1 mg, 72 %. Decomp. 107 °C. Elem. Anal. found: C, 19.09; H, 1.80; N, 9.19. Calc for $C_7H_7NAg_2N_2O_6$: C, 18.90; H, 1.59; N, 9.45.

Appendix

CRYSTALLOGRAPHY

Tables A1 – A14 list the crystal data and X-ray experimental details for fifty four crystal structures discussed in this thesis. Throughout the text, selected bond lengths and angles are discussed and listed under the appropriate figures, while the remaining distances and angles, as well as atomic coordinates are available on request from the Department of Chemistry, University of Canterbury.

The data for the crystal structures in this thesis was collected on a Bruker-Nonius APEX II system using graphite monochromatised Mo Kα (λ = 0.71073 Å) radiation at the temperature indicated in the following tables. The data collection, cell determination and data reduction were all performed with the APEX software. All structures had intensities corrected for Lorentz and polarization effects and for adsorption using SAINT. All structures were solved by direct methods using SHELXS and refined on F^2 using all data by full-matrix least squares procedures using SHELXL-97. Unless otherwise stated all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 and 1.5 times the isotropic equivalent of their carrier carbon atoms. Some of the refinements reported may change a little upon preparation for final publication.

Table A1. Crystal data and structure refinement for **2.10**, **2.11**, **2.12** and **2.13**.

Compound	**2.10**	**2.11**	**2.12**	**2.13**
Empirical formula	$C_{20}H_{20}O_8Cl_2Ag_2$	$C_{12}H_{14}F_4O_4SiAg$	$C_{20}H_{28}O_8F_{12}Ag_4$	$C_{15}H_{20}O_7ClAg$
Formula weight	675.00	500.61	1055.9	455.63
Temperature (K)	93(2)	122(2)	114(2)	93(2) K
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$	Pbam	P-1	$P2_1/c$
Unit cell dimensions: a(Å)	11.9236(7)	17.066(4)	8.4589(4)	8.5717(7)
b(Å)	13.3303(8)	7.820(1)	12.4826(5)	15.4778(13)
c(Å)	14.9791(9)	11.925(3)	13.5213(6)	13.6497(10)
α (°)	90	90	91.314(3)	90
β (°)	109.5540(10)	90	103.280(3)	93.4760(10)
γ (°)	90	90	92.719(3)	90
Volume ($Å^3$)	2243.5(2)	1591.6(6)	1387.1(1)	1807.6(2)
Z	4	4	2	4
Density (calculated) Mg/m^3	1.998	2.089	2.528	1.674
Absorption coefficient mm^{-1}	2.029	1.669	2.908	1.295
F(000)	1328	988	1016	920
Crystal size mm^3	0.36 x 0.32 x 0.18	0.65 x 0.30 x 0.02	0.29 x 0.20 x 0.04	0.58 x 0.56 x 0.28
Theta range for data collection (°)	1.81 to 26.42	1.71 to 25.05	1.55 to 25.05	2.38 to 25.05
Reflections collected	19242	21421	22117	13583
Independent reflections [R(int)]	4596 [0.0231]	1487 [0.0602]	4913 [0.0494]	3182 [0.0199]
Completeness to theta = 25.05° (%)	99.4	100	99.9	99.2
Data / restraints / parameters	4596 / 0 / 299	1487 / 0 / 121	4913 / 0 / 499	3182 / 0 / 219
Goodness-of-fit on F^2	1.628	1.874	1.136	1.097
Final R_1 indices [I>2sigma(I)]	0.0563	0.0745	0.0462	0.0176
wR_2 (all data)	0.1923	0.2633	0.167	0.0455
Largest diff. peak and hole ($e.Å^{-3}$)	3.601 and -1.543	1.098 and -2.402	1.451 and -2.270	0.288 and -0.410
Flack parameter where applicable				

Table A2. Crystal data and structure refinement for **2.14**, **2.15**, **2.16** and **2.17**.

Compound	**2.14**	**2.15**	**2.16**	**2.17**
Empirical formula	$B_2C_{24}H_{30}O_5F_8Ag_2$	$C_{12}H_{20}O_5F_6SiAg_2$	$C_{12}H_{16}O_7ClAg$	$C_{12}H_{16}O_3F_6PAg$
Formula weight	785.82	602.11	415.57	461.09
Temperature (K)	93(2)	115(2)	93(2)	93(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1$	P-1	P-1	P-1
Unit cell dimensions: a(Å)	6.4343(3)	7.0147(6)	7.3110(5)	7.3842(3)
b(Å)	18.8325(9)	10.5703(9)	10.2408(6)	10.5011(5)
c(Å)	11.8779(6)	12.7117(12)	10.4866(7)	10.7509(5)
α (°)	90	77.197(3)	81.638(3)	75.045(2)
β (°)	100.6350(10)	82.519(3)	70.703(3)	87.3270(10)
γ (°)	90	77.059(3)	89.436(3)	73.1820(10)
Volume ($Å^3$)	1414.57(12)	892.54(14)	732.53(8)	770.61(6)
Z	2	2	2	2
Density (calculated) Mg/m^3	1.845	2.24	1.884	1.987
Absorption coefficient mm^{-1}	1.471	2.342	1.587	1.486
F(000)	776	588	416	456
Crystal size mm^3	0.35 x 0.16 x 0.02	0.26 x 0.15 x 0.04	0.62 x 0.17 x 0.09	0.50 x 0.14 x 0.06
Theta range for data collection (°)	1.74 to 25.05	2.99 to 25.05	2.01 to 25.05	1.96 to 25.05
Reflections collected	10651	23996	5940	10978
Independent reflections [R(int)]	4810 [0.0258]	3175 [0.0405]	2564 [0.0179]	2709 [0.0229]
Completeness to theta = 25.05° (%)	96	99.8	98.6	99.3
Data / restraints / parameters	4810 / 1 / 370	3175 / 6 / 253	2564 / 0 / 198	2709 / 0 / 216
Goodness-of-fit on F^2	1.000	1.014	1.045	1.109
Final R_1 indices [I>2sigma(I)]	0.0223	0.0201	0.0213	0.0162
wR_2 (all data)	0.0542	0.0469	0.0584	0.0442
Largest diff. peak and hole ($e.Å^{-3}$)	0.556 and -0.522	0.662 and -0.539	0.790 and -0.573	0.386 and -0.292
Flack parameter where applicable	0.169(19)			

Table A3. Crystal data and structure refinement for **2.18**, **3.8**, **3.9** and **3.11**.

Compound	**2.18**	**3.8**	**3.9**	**3.11**
Empirical formula	$C_{13}H_{14}O_5F_3SAg$	$C_{16}H_{16}O_2$	$C_{16}H_{16}O_2$	$C_{16}H_{16}O_2$
Formula weight	447.17	240.29	240.29	240.29
Temperature (K)	127(2)	126(2)	93(2)	93(2)
Crystal system	Monoclinic	Orthorhomibc	Monoclinic	Monoclinic
Space group	$P2_1/c$	Pbca	$P2_1/c$	$P2_1$
Unit cell dimensions: a(Å)	5.256(2)	13.8548(8)	10.6608(9)	12.464(1)
b(Å)	20.810(15)	7.1534(4)	9.8120(8)	5.5935(6)
c(Å)	13.972(11)	26.810(1)	6.7922(5)	19.657(2)
α (°)	90	90	90	90
β (°)	91.30(2)	90	108.495(3)	106.779(4)
γ (°)	90	90	90	90
Volume ($Å^3$)	1527.8(17)	2657.1(3)	673.79(9)	1312.1(2)
Z	4	8	2	4
Density (calculated) Mg/m^3	1.944	1.201	1.184	1.216
Absorption coefficient mm^{-1}	1.51	0.078	0.077	0.079
F(000)	888	1024	256	512
Crystal size mm^3	0.60 x 0.03 x 0.03	0.65 x 0.53 x 0.02	0.71 x 0.22 x 0.11	0.51 x 0.34 x 0.15
Theta range for data collection (°)	1.96 to 25.05	2.94 to 25.04	2.01 to 25.05	1.08 to 25.05
Reflections collected	12513	26933	6238	11053
Independent reflections [R(int)]	2714 [0.1628]	2353 [0.1003]	834 [0.0400]	2585 [0.0455]
Completeness to theta = 25.05° (%)	99.9	99.8	0.7	99.9
Data / restraints / parameters	2714 / 0 / 208	2353 / 0 / 164	834 / 0 / 91	2585 / 1 / 325
Goodness-of-fit on F^2	0.961	0.966	1.615	1.152
Final R_1 indices [I>2sigma(I)]	0.0571	0.0477	0.0679	0.0475
wR_2 (all data)	0.1273	0.1637	0.2223	0.1273
Largest diff. peak and hole ($e.Å^{-3}$)	0.678 and -0.905	0.271 and -0.221	0.174 and -0.120	0.258 and -0.283
Flack parameter where applicable		0.0068(16)		0(10)

Table A4. Crystal data and structure refinement for **3.12**, **3.13**, **3.14b** and **3.15**.

Compound	**3.12**	**3.13**	**3.14b**	**3.15**
Empirical formula	$C_{16}H_{16}O_2$	$C_{16}H_{16}O_2$	$C_{26}H_{22}O_2$	$C_{16}H_{15}O_2$
Formula weight	240.29	240.29	366.44	239.28
Temperature (K)	93(2)	93(2)	111(2)	133(2)
Crystal system	Orthorhombic	Monoclinic	Tetragonal	Monoclinic
Space group	Pbcn	$P2_1/c$	$I4_1$	$P2_1/c$
Unit cell dimensions: a(Å)	25.331(2)	7.4056(8)	11.5925(2)	17.374(1)
b(Å)	7.1766(5)	22.315(2)	11.5925(2)	11.3558(9)
c(Å)	7.2090(4)	7.9224(8)	14.4706(5)	13.866(1)
α (°)	90	90	90	90
β (°)	90	99.639(7)	90	109.328(5)
γ (°)	90	90	90	90
Volume ($Å^3$)	1310.5(2)	1290.7(2)	1944.65(8)	2581.5(3)
Z	4	4	4	8
Density (calculated) Mg/m^3	1.218	1.237	1.252	1.231
Absorption coefficient mm^{-1}	0.079	0.08	0.078	0.08
F(000)	512	512	776	1016
Crystal size mm^3	0.31 x 0.13 x 0.06	0.25 x 0.17 x 0.09	0.46 x 0.31 x 0.09	0.48 x 0.27 x 0.14
Theta range for data collection (°)	1.61 to 25.05	1.83 to 25.05	2.48 to 25.05	1.24 to 25.05
Reflections collected	16151	9940	11582	13577
Independent reflections [R(int)]	1164 [0.0601]	2244 [0.0721]	903 [0.0412]	4484 [0.0665]
Completeness to theta = 25.05° (%)	99.5	98.2	99.9	97.7
Data / restraints / parameters	1164 / 0 / 83	2244 / 0 / 163	903 / 1 / 127	4484 / 0 / 325
Goodness-of-fit on F^2	0.968	0.999	1.126	0.982
Final R_1 indices [I>2sigma(I)]	0.0313	0.0494	0.0264	0.0584
wR_2 (all data)	0.0819	0.1137	0.0733	0.2041
Largest diff. peak and hole ($e.Å^{-3}$)	0.147 and -0.178	0.214 and -0.223	0.115 and -0.147	0.416 and -0.354
Flack parameter where applicable			0(10)	

Table A5. Crystal data and structure refinement for **3.16**, **3.17**, **3.18** and **3.20**.

Compound	**3.16**	**3.17**	**3.18**	**3.20**
Empirical formula	$C_{16}H_{16}O_6ClAg$	$C_{18}H_{16}O_8F_6S_2Ag_2$	$C_{34}H_{32}O_{10}F_6S_2Ag_2$	$C_{16}H_{16}O_{6½}ClAg$
Formula weight	447.61	754.17	994.46	455.61
Temperature (K)	93(2)	93(2)	96(2)	123(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	Cc	P-1	$P2_1/c$	P-1
Unit cell dimensions: a(Å)	8.315(2)	5.2220(3)	7.6515(3)	7.5921(4)
b(Å)	27.551(6)	9.5772(5)	25.044(1)	9.6150(7)
c(Å)	7.638(2)	12.3470(7)	8.9298(4)	11.9539(8)
α (°)	90	108.477(2)	90	71.357(3)
β (°)	113.53(3)	96.136(2)	96.195(2)	75.082(3)
γ (°)	90	103.923(2)	90	83.794(3)
Volume ($Å^3$)	1604.3(6)	557.10(5)	1701.2(1)	798.64(9)
Z	4	1	2	2
Density (calculated) Mg/m^3	1.853	2.248	1.941	1.895
Absorption coefficient mm^{-1}	1.453	2.041	1.367	1.463
F(000)	896	368	992	456
Crystal size mm^3	0.60 x 0.19 x 0.01	0.46 x 0.17 x 0.05	0.46 x 0.21 x 0.06	0.52 x 0.40 x 0.23
Theta range for data collection (°)	1.48 to 25.04	1.77 to 25.04	1.63 to 25.05	1.85 to 25.05
Reflections collected	5130	9076	16412	16716
Independent reflections [R(int)]	2070 [0.0536]	1966 [0.0214]	2999 [0.0416]	2816 [0.0315]
Completeness to theta = 25.05° (%)	100	99.1	99.6	99.5
Data / restraints / parameters	2070 / 2 / 225	1966 / 0 / 163	2999 / 0 / 244	2816 / 0 / 280
Goodness-of-fit on F^2	1.072	1.074	0.753	1.003
Final R_1 indices [I>2sigma(I)]	0.053	0.014	0.024	0.0344
wR_2 (all data)	0.1346	0.0389	0.0921	0.0907
Largest diff. peak and hole ($e.Å^{-3}$)	1.548 and -1.482	0.464 and -0.357	0.464 and -0.389	0.537 and -0.443
Flack parameter where applicable	0.07(8)			

Table A6. Crystal data and structure refinement for **3.20**, **3.21**, **3.22** and **3.23**.

Compound	**3.20**	**3.21**	**3.22**	**3.23**
Empirical formula	$C_{16}H_{16}O_2F_6PAg$	$BC_{16}H_{16}O_2F_4Ag$	$C_{17}H_{16}O_5F_3SAg$	$C_{26}H_{22}O_{10}Cl_2Ag_2$
Formula weight	493.13	434.97	497.23	573.76
Temperature (K)	93(2)	113(2)	93(2)	93(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$	P-1	$P2_1/c$
Unit cell dimensions: a(Å)	9.3991	6.4654(5)	7.1311(5)	7.3058(8)
b(Å)	9.5536(7)	17.356(1)	10.5430(7)	22.389(3)
c(Å)	10.0534(7)	14.436(1)	12.5105(8)	23.483(3)
α (°)	103.465(4)	90	88.233(3)	90
β (°)	91.612(4)	93.275(5)	77.423(3)	92.650(6)
γ (°)	103.068(4)	90	77.325(3)	90
Volume ($Å^3$)	852.1(1)	1617.3(2)	895.5(1)	3837.0(8)
Z	2	4	2	6
Density (calculated) Mg/m^3	1.922	1.786	1.844	1.49
Absorption coefficient mm^{-1}	1.347	1.294	1.299	0.93
F(000)	488	864	496	1740
Crystal size mm^3	0.16 x 0.12 x 0.06	0.30 x 0.10 x 0.03	0.33 x 0.10 x 0.07	0.83 x 0.04 x 0.04
Theta range for data collection (°)	2.09 to 25.02	1.84 to 25.05	3.21 to 25.00	1.26 to 25.05
Reflections collected	10852	16686	6711	61421
Independent reflections [R(int)]	3004 [0.0462]	2710 [0.2188]	3000 [0.0516]	6783 [0.1169]
Completeness to theta = 25.05° (%)	100	94.7	94.8	99.9
Data / restraints / parameters	3004 / 86 / 304	2710 / 0 / 217	3000 / 0 / 244	6783 / 0 / 496
Goodness-of-fit on F^2	1.060	3.32	1.058	3.079
Final R_1 indices [I>2sigma(I)]	0.0532	0.2268	0.0259	0.1966
wR_2 (all data)	0.1182	0.4912	0.0644	0.4808
Largest diff. peak and hole ($e.Å^{-3}$)	1.015 and -0.932	3.631 and -3.556	0.559 and -0.564	4.126 and -2.064
Flack parameter where applicable				

Table A7. Crystal data and structure refinement for **3.24**, **4.17**, **4.18** and **4.19**.

Compound	**3.24**	**4.17**	**4.18**	**4.19**
Empirical formula	$C_{26}H_{22}O_{10}Cl_2Ag_2$	$C_{24}H_{26}O_{13}Cl_3Ag_3$	$C_{14}H_{14}O_8Cl_2Ag_2$	$C_{14}H_{14}O_{16}Cl_4Ag_4$
Formula weight	573.76	952.41	596.89	1011.53
Temperature (K)	94(2)	115(2)	93(2)	114(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	C2	P2/c	Pmna	P-1
Unit cell dimensions: a(Å)	39.349(2)	17.9872(12)	10.9051(18)	7.9740(2)
b(Å)	7.4991(4)	5.5107(3)	5.9532(9)	9.3990(3)
c(Å)	10.2915(7)	16.1980(10)	13.215(2)	9.9397(3)
α (°)	90	90	90	63.445(2)
β (°)	101.951(6)	97.506(2)	90	72.188(2)
γ (°)	90	90	90	71.841(2)
Volume ($Å^3$)	2971.1(3)	1591.82(17)	857.9(2)	620.90(3)
Z	4	2	2	1
Density (calculated) Mg/m^3	1.283	1.987	2.311	2.705
Absorption coefficient mm^{-1}	0.8	2.14	2.636	3.614
F(000)	1160	932	580	482
Crystal size mm^3	0.53 x 0.04 x 0.03	0.72 x 0.22 x 0.20	0.40 x 0.05 x 0.04	0.40 x 0.13 x 0.03
Theta range for data collection (°)	1.06 to 25.04	2.64 to 25.05	2.42 to 30.55	2.66 to 25.04
Reflections collected	14168	26570	12345	6734
Independent reflections [R(int)]	4972 [0.0641]	2825 [0.0307]	1338 [0.0433]	2184 [0.0198]
Completeness to theta = 25.05° (%)	99.9	99.8	97.7	99.1
Data / restraints / parameters	4972 / 1 / 380	2825 / 1 / 214	1338 / 0 / 66	2184 / 0 / 172
Goodness-of-fit on F^2	1.709	1.222	1.037	1.073
Final R_1 indices [I>2sigma(I)]	0.1125	0.0438	0.0395	0.0242
wR_2 (all data)	0.2922	0.1287	0.1134	0.0796
Largest diff. peak and hole ($e.Å^{-3}$)	1.568 and -2.453	1.838 and -0.901	1.746 and -0.642	0.834 and -1.088
Flack parameter where applicable	0.09(11)			

Table A8. Crystal data and structure refinement for **4.20**, **4.21**, **4.22** and **4.23**.

Compound	**4.20**	**4.21**	**4.22**	**4.23**
Empirical formula	$B_4C_{24}H_{30}OF_{16}Ag_4$	$C_{22}H_{22}O_{12}F_{12}S_4Ag_4$	$C_{24}H_{32}O_4F_{12}P_2Ag_2$	$C_{20}H_{20}O_8F_6S_2Ag_2$
Formula weight	1129.32	1266.12	890.18	782.22
Temperature (K)	113(2)	123(2)	156(2)	163(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	Pnma	P2/n	P-1	$P2_1/c$
Unit cell dimensions: a(Å)	20.443(3)	18.610(4)	8.178(5)	8.5565(6)
b(Å)	23.264(4)	5.0352(7)	9.751(3)	17.1574(13)
c(Å)	7.775(1)	19.387(4)	10.673(5)	8.8201(6)
α (°)	90	90	84.10(2)	90
β (°)	90	101.632(4)	67.652(10)	98.202(4)
γ (°)	90	90	84.29(2)	90
Volume ($Å^3$)	3697.6(1)	1779.3(6)	781.3(6)	1281.61(16)
Z	4	2	1	2
Density (calculated) Mg/m^3	2.029	2.363	1.892	2.027
Absorption coefficient mm^{-1}	2.188	2.523	1.457	1.778
F(000)	2200	1220	440	768
Crystal size mm^3	0.15 x 0.10 x 0.02	0.51 x 0.06 x 0.01	0.54 x 0.25 x 0.05	0.46 x 0.10 x 0.10
Theta range for data collection (°)	1.75 to 30.49	1.38 to 25.05	2.07 to 25.05	2.37 to 25.04
Reflections collected	33925	34875	10063	32956
Independent reflections [R(int)]	5724 [0.1960]	3130 [0.0950]	2748 [0.0370]	2273 [0.0651]
Completeness to theta = 25.05° (%)	99.4	99.9	99	100
Data / restraints / parameters	5724 / 0 / 113	3130 / 0 / 244	2748 / 0 / 201	2273 / 0 / 172
Goodness-of-fit on F^2	1.376	1.140	0.962	1.117
Final R_1 indices [I>2sigma(I)]	0.1733	0.042	0.0407	0.0318
wR_2 (all data)	0.5154	0.1743	0.1251	0.0924
Largest diff. peak and hole ($e.Å^{-3}$)	10.066 and -4.169	0.848 and -1.558	0.885 and -0.534	0.638 and -0.918
Flack parameter where applicable	0.0001(3)			

Table A9. Crystal data and structure refinement for **4.24**, **4.25**, **5.10** and **5.11**.

Compound	**4.24**	**4.25**	**5.10**	**5.11**
Empirical formula	$C_{24}H_{32}O_{12}Cl_2Ag_2$	$C_{24}H_{34}O_4F_{12}P_2Ag_2$	$C_8H_{16}O_{10}F_6S_2Ag_2$	$C_9H_{15}NO_4ClAg$
Formula weight	801.16	892.19	666.06	344.54
Temperature (K)	107(2)	96(2)	119(2)	119(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	Pbcm	$P2_1$
Unit cell dimensions: a(Å)	14.1458(6)	9.7436(4)	11.535(1)	7.7830(4)
b(Å)	8.0431(3)	11.1157(4)	14.239(2)	9.6733(4)
c(Å)	12.9056(5)	14.3871(5)	12.1003(8)	8.0976(4)
α (°)	90	90	90	90
β (°)	92.015(2)	95.597(2)	90	103.250(2)
γ (°)	90	90	90	90
Volume ($Å^3$)	1467.44(10)	1550.8(1)	1987.5(3)	593.42(5)
Z	2	2	4	2
Density (calculated) Mg/m^3	1.813	1.911	2.226	1.928
Absorption coefficient mm^{-1}	1.576	1.468	2.278	1.921
F(000)	804	884	1296	344
Crystal size mm^3	0.54 x 0.38 x 0.19	0.24 x 0.15 x 0.02	0.45 x 0.19 x 0.06	0.24 x 0.20 x 0.11
Theta range for data collection (°)	1.44 to 25.04	2.79 to 25.04	2.83 to 25.05	2.58 to 25.02
Reflections collected	24962	16598	10051	7418
Independent reflections [R(int)]	2590 [0.0385]	2746 [0.0455]	1841 [0.0270]	2097 [0.0576]
Completeness to theta = 25.05° (%)	99.4	99.8	99.3	99.9
Data / restraints / parameters	2590 / 0 / 191	2746 / 0 / 200	1841 / 4 / 172	2097 / 1 / 145
Goodness-of-fit on F^2	0.925	1.174	1.031	0.957
Final R_1 indices [I>2sigma(I)]	0.0284	0.0339	0.0348	0.0557
wR_2 (all data)	0.1006	0.0893	0.1033	0.131
Largest diff. peak and hole ($e.Å^{-3}$)	0.903 and -0.816	0.837 and -0.621	1.675 and -0.922	0.839 and -0.734
Flack parameter where applicable				0.53(8)

Table A10. Crystal data and structure refinement for **5.12**, **5.13**, **5.14** and **5.15**.

Compound	**5.12**	**5.13**	**5.14**	**5.15**
Empirical formula	$C_9H_{15}NF_6PAg$	$C_{10}H_{15}NO_3F_3SAg$	$C_9H_{14}N_2O_3Ag$	$C_{17}H_{28}O_{16}Cl_4Ag_4$
Formula weight	390.06	394.16	306.09	711.04
Temperature (K)	103(2)	105(2)	98(2)	93(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Tetragonal
Space group	$Pna2_1$	$Pna2_1$	$P2_1/n$	I-42d
Unit cell dimensions: a(Å)	13.7975(5)	14.0842(7)	8.7549(3)	18.3158(5)
b(Å)	9.7750(3)	10.3590(5)	9.8295(3)	18.3158(5)
c(Å)	9.5428(3)	9.5834(5)	12.9082(4)	7.0783(3)
α (°)	90	90	90	90
β (°)	90	90	90.423(2)	90
γ (°)	90	90	90	90
Volume ($Å^3$)	1287.04(7)	1398.20(12)	1110.80(6)	2374.55(14)
Z	4	4	4	8
Density (calculated) Mg/m^3	2.013	1.872	1.83	1.989
Absorption coefficient mm^{-1}	1.744	1.627	1.804	1.93
F(000)	768	784	612	1416
Crystal size mm^3	0.60 x 0.60 x 0.09	0.46 x 0.09 x 0.02	0.60 x 0.18 x 0.07	0.78 x 0.27 x 0.21
Theta range for data collection (°)	2.55 to 25.03	2.89 to 25.05	2.60 to 25.05	3.09 to 25.02
Reflections collected	8457	15179	16591	7762
Independent reflections [R(int)]	2007 [0.0543]	2324 [0.0549]	1476 [0.0264]	1050 [0.1651]
Completeness to theta = 25.05° (%)	99.5	94.3	74.8	99.8
Data / restraints / parameters	2007 / 1 / 163	2324 / 1 / 162	1476 / 0 / 136	1050 / 6 / 95
Goodness-of-fit on F^2	0.685	0.735	1.079	0.922
Final R_1 indices [I>2sigma(I)]	0.0245	0.0272	0.0178	0.0205
wR_2 (all data)	0.0768	0.0974	0.0537	0.0558
Largest diff. peak and hole ($e.Å^{-3}$)	0.754 and -0.761	0.432 and -0.444	0.678 and -0.588	0.546 and -0.284
Flack parameter where applicable	-0.02(3)	0.05(6)		-0.06(4)

Table A11. Crystal data and structure refinement for **6.16**, **6.17**, **6.18** and **6.19**.

Compound	**6.16**	**6.17**	**6.18**	**6.19**
Empirical formula	$C_{32}H_{36}O_{20}N_4Cl_4Ag_4$	$C_{18}H_{18}O_8F_6S_2Ag_2$	$C_{16}H_{18}N_2O_{10}Cl_2Ag_2$	C_8H_9NOCuI
Formula weight	1369.92	784.2	684.96	325.6
Temperature (K)	117(2)	124(2)	124(2)	93(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P-1	C2/c	$P2_1/c$
Unit cell dimensions: a(Å)	10.7975(11)	8.708(2)	19.414(2)	13.7062(7)
b(Å)	13.6846(14)	8.916(2)	9.7792(14)	4.2019(2)
c(Å)	14.7445(15)	9.259(2)	14.0838(19)	18.2485(9)
α (°)	90	99.68(1)	90	90
β (°)	106.198(2)	93.24(2)	125.740(6)	111.313(3)
γ (°)	90	112.69(1)	90	90
Volume ($Å^3$)	2092.2(4)	647.9(2)	2170.4(5)	979.09(8)
Z	2	1	4	4
Density (calculated) Mg/m^3	2.175	2.01	2.096	2.209
Absorption coefficient mm^{-1}	2.186	1.761	2.108	5.335
F(000)	1344	384	1344	616
Crystal size mm^3	0.60 x 0.10 x 0.09	0.52 x 0.21 x 0.11	0.23 x 0.23 x 0.20	0.76 x 0.06 x 0.03
Theta range for data collection (°)	2.46 to 25.05	2.25 to 25.05	2.55 to 25.05	1.59 to 25.10
Reflections collected	9813	6703	5968	11622
Independent reflections [R(int)]	1860 [0.0337]	2096 [0.1052]	1914 [0.0297]	1724 [0.0866]
Completeness to theta = 25.05° (%)	99.9	91.2	99.7	0.999
Data / restraints / parameters	1860 / 0 / 165	2096 / 0 / 172	1914 / 0 / 145	1724 / 0 / 137
Goodness-of-fit on F^2	1.384	1.086	1.079	1.169
Final R_1 indices [I>2sigma(I)]	0.0228	0.0699	0.0294	0.0313
wR_2 (all data)	0.0638	0.1897	0.0652	0.1517
Largest diff. peak and hole ($e.Å^{-3}$)	0.299 and -0.899	0.824 and -0.963	0.802 and -0.501	1.781 and -1.396
Flack parameter where applicable				

Table A12. Crystal data and structure refinement for **6.20**, **6.21**, **6.22** and **6.23**.

Compound	**6.20**	**6.21**	**6.22**	**6.23**
Empirical formula	$C_8H_9NO_5ClAg$	$C_8H_9NOF_6PAg$	$C_{22}H_{26}N_2O_{16}Cl_3Ag_3$	$C_{11}H_{13}NO_2Cl_2Cu_2$
Formula weight	342.48	388	1004.4	389.2
Temperature (K)	143(2)	110(2)	143(2)	120(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	Pbca	Pbca	C2/c	P-1
Unit cell dimensions: a(Å)	14.877(2)	9.6530(7)	23.939(3)	7.652(2)
b(Å)	9.1792(10)	15.3790(13)	7.6319(6)	8.245(2)
c(Å)	15.807(2)	15.9992(14)	17.115(2)	11.036(3)
α (°)	90	90	90	82.241(9)
β (°)	90	90	98.650(3)	77.507(8)
γ (°)	90	90	90	73.920(9)
Volume ($Å^3$)	2158.6(5)	2375.1(3)	3091.4(6)	651.1(3)
Z	8	8	4	2
Density (calculated) Mg/m^3	2.108	2.17	2.158	1.985
Absorption coefficient mm^{-1}	2.119	1.896	2.218	3.666
F(000)	1344	1504	1968	388
Crystal size mm^3	0.57 x 0.33 x 0.05	0.58 x 0.15 x 0.03	0.63 x 0.11 x 0.03	0.21 x 0.06 x 0.01
Theta range for data collection (°)	2.58 to 25.04	2.55 to 25.05	1.72 to 25.05	2.82 to 25.05
Reflections collected	45957	32527	20226	8056
Independent reflections [R(int)]	1908 [0.0455]	2104 [0.0749]	2725 [0.0532]	2260 [0.0655]
Completeness to theta = 25.05° (%)	100	99.9	99.9	98.3
Data / restraints / parameters	1908 / 0 / 145	2104 / 0 / 163	2725 / 0 / 209	2260 / 0 / 163
Goodness-of-fit on F^2	1.121	1.055	1.189	0.996
Final R_1 indices [I>2sigma(I)]	0.0417	0.0412	0.0385	0.0446
wR_2 (all data)	0.1188	0.1091	0.0912	0.1102
Largest diff. peak and hole ($e.Å^{-3}$)	0.989 and -0.671	1.127 and -1.076	1.071 and -0.758	1.037 and -0.583
Flack parameter where applicable				

Table A13. Crystal data and structure refinement for **6.24**, **6.25**, **6.26** and **6.27**.

Compound	**6.24**	**6.25**	**6.26**	**6.27**
Empirical formula	$C_{18}H_{18}O_8F_6S_2Ag_2$	$C_{16}H_{18}N_2O_2F_{12}P_2Ag_2$	$C_{16}H_{18}N_2O_{10}Cl_2Ag_2$	$C_7H_7N_3O_6Ag_2$
Formula weight	784.2	776	684.96	444.9
Temperature (K)	106(2)	98(2)	123(2)	108(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions: a(Å)	6.0480(3)	9.6216(3)	9.5057(3)	6.9352(4)
b(Å)	8.9116(4)	13.2017(5)	12.9244(5)	14.8039(9)
c(Å)	11.5147(5)	9.7745(3)	9.1236(3)	10.4456(5)
α (°)	77.202(2)	90	90	90
β (°)	82.796(2)	112.789(2)	111.0570(10)	99.769(2)
γ (°)	83.254(2)	90	90	90
Volume ($Å^3$)	597.83(5)	1144.65(7)	1046.04(6)	1056.88(10)
Z	1	2	2	4
Density (calculated) Mg/m^3	2.178	2.251	2.175	2.796
Absorption coefficient mm^{-1}	1.909	1.967	2.186	3.731
F(000)	384	752	672	848
Crystal size mm^3	0.32 x 0.30 x 0.13	0.66 x 0.50 x 0.20	0.59 x 0.39 x 0.11	0.75 x 0.33 x 0.29
Theta range for data collection (°)	1.82 to 25.04	2.74 to 25.05	2.30 to 25.04	2.75 to 30.60
Reflections collected	16119	29743	6145	37872
Independent reflections [R(int)]	2119 [0.0351]	2035 [0.0261]	1853 [0.0217]	3215 [0.0387]
Completeness to theta = 25.05° (%)	100	100	99.9	99
Data / restraints / parameters	2119 / 0 / 182	2035 / 0 / 163	1853 / 0 / 230	3215 / 0 / 173
Goodness-of-fit on F^2	1.331	0.811	0.96	1.166
Final R_1 indices [I>2sigma(I)]	0.0178	0.0165	0.0258	0.0232
wR_2 (all data)	0.0721	0.0834	0.1084	0.057
Largest diff. peak and hole ($e.Å^{-3}$)	0.628 and -0.504	0.426 and -0.794	0.558 and -0.612	1.107 and -1.139
Flack parameter where applicable				

Table A14. Crystal data and structure refinement for **6.29**.

Compound	**6.29**	**6.29**
Empirical formula	$C_{28}H_{28}N_4O_8Cl_2Pd$	$C_{28}H_{28}N_4O_8Cl_2Pd$
Formula weight	796.79	725.84
Temperature (K)	117(2)	119(2)
Crystal system	Rhombohedral	Triclinic
Space group	R-3	P-1
Unit cell dimensions: a(Å)	27.1943(5)	11.1982(2)
b(Å)	27.1943(5)	15.1142(4)
c(Å)	11.6998(4)	16.2623(4)
α (°)	90	105.550(1)
β (°)	90	96.882(1)
γ (°)	120	105.115(1)
Volume ($Å^3$)	7493.2(3)	2506.1(1)
Z	9	3
Density (calculated) Mg/m^3	1.448	1.443
Absorption coefficient mm^{-1}	0.77	0.765
F(000)	3312	1104
Crystal size mm^3	0.84 x 0.25 x 0.20	0.34 x 0.27 x 0.14
Theta range for data collection (°)	1.50 to 30.54	1.64 to 25.05
Reflections collected	86582	39389
Independent reflections [R(int)]	5092 [0.0545]	8855 [0.0368]
Completeness to theta = 25.05° (%)	99.7	99.9
Data / restraints / parameters	5092 / 0 / 196	8855 / 0 / 578
Goodness-of-fit on F^2	1.12	1.08
Final R_1 indices [I>2sigma(I)]	0.0858	0.0645
wR_2 (all data)	0.3235	0.2155
Largest diff. peak and hole ($e.Å^{-3}$)	6.879 and -1.246	4.244 and -1.599
Flack parameter where applicable		

References

REFERENCES

(1) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
(2) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; John Wiley & Sons Ltd: New York, 2000.
(3) Constable, E. C. *Chemistry and Industry* **1994**, 56 - 60.
(4) Steel, P. J. *Chemistry in New Zealand* **2003**, 57 - 60.
(5) Lindoy, L. F.; Atkinson, I. M. *Self-Assembly in Supramolecular Systems*; Cambridge University Press: Cambridge, UK, 2000.
(6) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chemical Reviews* **2000**, *100*, 853-908.
(7) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chemical Reviews* **1997**, *97*, 2005-2062.
(8) Albrecht, M. *Chemical Reviews* **2001**, *101*, 3457-3498.
(9) Swiegers, G. F.; Malefetse, T. J. *Chemical Reviews* **2000**, *100*, 3483-3538.
(10) Yuan, J.-X.; Hu, M.-L.; Cheng, Y.-Q.; Chena, L.-C.; Ng, S. W. *Acta Crystallographica Section C-Crystal Structure Communications* **2002**, *58*, m270-m272.
(11) Haddad, M. S.; Hendrickson, D. N.; Cannady, J. P.; Drago, R. S.; Bieksza, D. S. *Journal of the American Chemical Society* **1979**, *101*, 898-906.
(12) Darriet, J.; Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Inorganic Chemistry* **1979**, *18*, 2679-2682.
(13) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angewandte Chemie International Edition in English* **1995**, *34*, 1895-1898.
(14) Lau, V. C.; Berben, L. A.; Long, J. R. *Journal of the American Chemical Society* **2002**, *124*, 9042-9043.
(15) Steel, P. J.; Fitchett, C. M. *Coordination Chemistry Reviews* **2008**, *252*, 990-1006.
(16) Shriver, D. F.; Atkins, P. W. *Inorganic Chemistry*; 3rd ed.; W. H. Freeman and Co., 1999.
(17) Lindner, E.; Hermann, C.; Baum, G.; Fenske, D. *European Journal of Inorganic Chemistry* **1999**, *1999*, 679-685.
(18) James, S. L.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Chemical Communications* **1998**, 2323-2324.
(19) Mahmoudkhani, A. H.; Cote, A. P.; Shimizu, G. K. H. *Chemical Communications* **2004**, 2678-2679.
(20) Cooper, G. J. T.; Abbas, H.; Kogerler, P.; Long, D.-L.; Cronin, L. *Inorganic Chemistry* **2004**, *43*, 7266-7268.
(21) Saalfrank, R. W.; Glaser, H.; Demleitner, B.; Hampel, F.; Chowdhry, M. M.; Schünemann, V.; Trautwein, A. X.; Vaughan, G. B. M.; R., Y.; Davis, A. V.; KRaymond, K. N. *Chemistry - A European Journal* **2002**, *8*, 493-497.
(22) Chadha, R.; Kumar, R.; Tuck, D. G. *Journal of the Chemical Society, Chemical Communications* **1986**, 188 - 189.

(23) Seyferth, D. *Organometallics* **2001**, *20*, 2-6.
(24) Dewar, M. J. S. *Bulletin de la Societe Chimique de France* **1951**, *18*, C71-C79.
(25) Winterton, N. In *International Conference on Coordination Chemistry* Cambridge, 2002, p 103 - 110.
(26) Ziegler, T.; Rauk, A. *Inorganic Chemistry* **1979**, *18*, 1558-1565.
(27) Hertwig, R. H.; Koch, W.; Schroder, D.; Schwarz, H.; Hrusak, J.; Schwerdtfeger, P. *Journal of Physical Chemistry* **1996**, *100*, 12253-12260.
(28) Manard, M. J.; Kemper, P. R.; Bowers, M. T. *International Journal of Mass Spectrometry* **2005**, *241*, 109-117.
(29) Ivanov, S. V.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Crystal Growth & Design* **2004**, *4*, 249-254.
(30) Dargel, T. K.; Hertwig, R. H.; Koch, W. *Molecular Physics* **1999**, *96*, 583-591.
(31) Eriksson, L.; Kritikos, M. *Acta Crystallographica Section C-Crystal Structure Communications* **1995**, *51*, 1508-1510.
(32) Amma, E. L.; Griffith, E. A. H. *Journal of the American Chemical Society* **1971**, *93*, 3167-3172.
(33) Rundle, R. E.; Goring, J. H. *Journal of the American Chemical Society* **1950**, *72*, 5337.
(34) Wadepohl, H.; Pritzkow, H. *Acta Crystallographica Section C-Crystal Structure Communications* **2001**, *57*, 383-384.
(35) Smith, H. G.; Rundle, R. E. *Journal of the American Chemical Society* **1958**, *80*, 5075-80.
(36) McMullan, R. K.; Koetzle, T. F.; Fritchie, C. J. *Acta Crystallographica Section B-Structural Science* **1997**, *53*, 645-653.
(37) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *Journal of the American Chemical Society* **1985**, *107*, 1979-1985.
(38) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *Journal of the American Chemical Society* **1985**, *107*, 5955-5959.
(39) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G. L.; Kojima, T. *Journal of the American Chemical Society* **1998**, *120*, 8610-8618.
(40) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067-1079.
(41) Koschabek, R.; Gleiter, R.; Rominger, F. *European Journal of Inorganic Chemistry* **2006**, *2006*, 609-620.
(42) Schmidbaur, H.; Bublak, W.; Huber, B.; Reber, G.; Müller, G. *Angewandte Chemie International Edition in English* **1986**, *25*, 1089-1090.
(43) Wang, Q.-M.; Mak, T. C. W. *Chemical Communications* **2002**, 2682-2683.
(44) Xu, F.-B.; Li, Q.-S.; Wu, L.-Z.; Leng, X.-B.; Li, Z.-C.; Zeng, X.-S.; Chow, Y. L.; Zhang, Z.-Z. *Organometallics* **2003**, *22*, 633-640.
(45) Xu, F.-B.; Weng, L.-H.; Sun, L.-J.; Zhang, Z.-Z.; Zhou, Z.-F. *Organometallics* **2000**, *19*, 2658-2660.

(46) Mascal, M.; Kerdelhué, J.-L.; Blake, A. J.; Cooke, P. A. *Angewandte Chemie International Edition* **1999**, *38*, 1968-1971.
(47) Wen, M.; Munakata, M.; Suenaga, Y.; Kuroda-Sowa, T.; Maekawa, M. *Inorganica Chimica Acta* **2002**, *332*, 18-24.
(48) Zhong, J. C.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Konaka, H. *Inorganica Chimica Acta* **2001**, *322*, 150-156.
(49) Elliott, E. L.; Hernandez, G. A.; Linden, A.; Siegel, J. S. *Organic & Biomolecular Chemistry* **2005**, *3*, 407-413.
(50) Munakata, M.; Wu, L. P.; Ning, G. L. *Coordination Chemistry Reviews* **2000**, *198*, 171-203.
(51) Wen, M.; Munakata, M.; Li, Y.-Z.; Suenaga, Y.; Kuroda-Sowa, T.; Maekawa, M.; Anahata, M. *Polyhedron* **2007**, *26*, 2455-2460.
(52) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ohta, T.; Konaka, H. *Inorganic Chemistry* **2003**, *42*, 2553-2558.
(53) Winstein, S.; Lucas, H. J. *Journal of the American Chemical Society* **1938**, *60*, 836-847.
(54) Quinn, H. W. *Canadian Journal of Chemistry* **1967**, *45*, 1329-36.
(55) Quinn, H. W. *Canadian Journal of Chemistry* **1968**, *46*, 117-24.
(56) Quinn, H. W.; Glow, D. N. *Canadian Journal of Chemistry* **1962**, *40*, 1103-12.
(57) Quinn, H. W.; McIntyre, J. S.; Peterson, D. J. *Canadian Journal of Chemistry* **1965**, *43*, 2896-910.
(58) Quinn, H. W.; Tsai, J. H. *Advances in Inorganic Chemistry and Radiochemistry* **1969**, *12*, 217-373.
(59) Quinn, H. W.; VanGilder, R. L. *Canadian Journal of Chemistry* **1969**, *47*, 4691-4.
(60) Quinn, H. W.; VanGilder, R. L. *Canadian Journal of Chemistry* **1970**, *48*, 2435-7.
(61) Quinn, H. W.; VanGilder, R. L. *Canadian Journal of Chemistry* **1971**, *49*, 1323-7.
(62) Dias, H. V. R.; Wang, X. *Dalton Transactions* **2005**, 2985-2987.
(63) Dias, H. V. R.; Fianchini, M. *Angewandte Chemie International Edition* **2007**, *46*, 2188-2191.
(64) Dias, H. V. R.; Wu, J.; Wang, X.; Rangan, K. *Inorganic Chemistry* **2007**, *46*, 1960-1962.
(65) Dias, H. V. R.; Wang, Z.; Jin, W. *Inorganic Chemistry* **1997**, *36*, 6205-6215.
(66) Chiong, H. A.; Daugulis, O. *Organometallics* **2006**, *25*, 4054-4057.
(67) Baenziger, N. C.; Haight, H. L.; Alexander, R.; Doyle, J. R. *Inorganic Chemistry* **1966**, *5*, 1399-1400.
(68) Traynham, J. G.; Olechowski, J. R. *Journal of the American Chemical Society* **1959**, *81*, 571-574.
(69) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *Journal of the Chemical Society B: Physical Organic* **1959**, 3178 - 3182.
(70) Traynham, J. G. *The Journal of Organic Chemistry* **1961**, *26*, 4694-4696.

(71) Lim, K. C.; Marchetti, F.; Pettinari, C.; Skelton, B. W.; Smith, B. J.; White, A. H. *Inorganica Chimica Acta* **2006**, *359*, 1594-1602.
(72) Caughlan, C. N.; Smith, G. D.; Jennings, P. W.; Voecks, G. E. *Acta Crystallographica. Section B-Structural Crystallography and Crystal Chemistry*. **1976**, 1390 - 1393.
(73) Rencken, I.; Boeyens, J. C. A.; Orchard, S. W. *Journal of Chemical Crystallography* **1988**, *18*, 293-306.
(74) Doppelt, P.; Baum, T. H.; Ricard, L. *Inorganic Chemistry* **1996**, *35*, 1286-1291.
(75) Mathews, F. S.; Lipscomb, W. N. *Journal of Physical Chemistry* **1959**, *63*, 845-850.
(76) Jackson, R. B.; Streib, W. E. *Journal of the American Chemical Society* **1967**, *89*, 2539-2543.
(77) Hossain, M. B.; Van der Helm, D. *Journal of the American Chemical Society* **1968**, *90*, 6607-6611.
(78) Allen, F. H.; Rogers, D. *Journal of the Chemical Society B: Physical Organic* **1971**, 257 - 262.
(79) Faure, R.; Loiseleur, H.; Haufe, G.; Trauer, H. *Acta Crystallographica Section C-Crystal Structure Communications* **1985**, *41*, 1593-1595.
(80) Mitsudo, T.-a.; Suzuki, T.; Zhang, S.-W.; Imai, D.; Fujita, K.-i.; Manabe, T.; Shiotsuki, M.; Watanabe, Y.; Wada, K.; Kondo, T. *Journal of the American Chemical Society* **1999**, *121*, 1839-1850.
(81) Williams, C. M.; Mander, L. N. *Tetrahedron* **2001**, *57*, 425-447.
(82) van Beek, T. A.; Subrtova, D. *Phytochemical Analysis* **1995**, *6*, 1-19.
(83) Futterer, T.; Merz, A.; Lex, J. *Angewandte Chemie International Edition in English* **1997**, *36*, 611-613.
(84) Prince, P. D.; Steed, J. W.; Cragg, P. J. *Chemical Communications* **1999**, 1179 - 1180.
(85) Arya, P.; Channa, A.; Cragg, P. J.; Prince, P. D.; Steed, J. W. *New Journal of Chemistry* **2002**, *26*, 440-447.
(86) Yoshida, T.; Kuwatani, Y.; Hara, K.; Yoshida, M.; Matsuyama, H.; Iyoda, M.; Nagase, S. *Tetrahedron Letters* **2001**, *42*, 53-56.
(87) Kuwatani, Y.; Yoshida, T.; Kusaka, A.; Oda, M.; Hara, K.; Yoshida, M.; Matsuyama, H.; Iyoda, M. *Tetrahedron* **2001**, *57*, 3567-3576.
(88) Kuwatani, Y.; Yoshida, T.; Hara, K.; Yoshida, M.; Matsuyama, H.; Iyoda, M. *Organic Letters* **2000**, *2*, 4017-4020.
(89) Evans, W. J.; Giarikos, D. G.; Josell, D.; Ziller, J. W. *Inorganic Chemistry* **2003**, *42*, 8255-8261.
(90) Chi, K.-M.; Chen, K.-H.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1996**, *15*, 2575-2578.
(91) Xu, C.; Corbitt, T. S.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Journal of the Chemical. Society, Dalton Transactions* **1994**, 2841 - 2849,.
(92) Edwards, D. A.; Mahon, M. F.; Molloy, K. C.; Ogrodnik, V. *Journal of Materials Chemistry* **2003**, *13*, 563-570.
(93) Steel, P. J.; Webb, N. C. *European Journal of Inorganic Chemistry* **2002**, *2002*, 2257-2260.

(94) Cottam, J. R. A.; Steel, P. J. *Journal of Organometallic Chemistry* **2006**, *691*, 2286-2290.
(95) Burgess, J.; Cottam, J. R. A.; Steel, P. J. *Australian Journal of Chemistry* **2006**, *59*, 295-297.
(96) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *Journal of the American Chemical Society* **1994**, *116*, 1151-1152.
(97) Biradha, K.; Fujita, M. *Journal of the Chemical Society, Dalton Transactions* **2000**, 3805-3810.
(98) Halder, P.; Ranjan, P.; Ennio, B.; Tapan, Z.; , K. *European Journal of Inorganic Chemistry* **2008**, 5659-5665.
(99) Rodesiler, P. F.; Griffith, E. A. H.; Amma, B. L. *Journal of the American Chemical Society* **1972**, *94*, 761-766.
(100) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Transactions* **2007**, 955-964.
(101) Bosch, E.; Barnes, C. L. *Inorganic Chemistry* **2002**, *41*, 2543-2547.
(102) Dance, I. G.; Fitzpatrick, L. J.; Rae, A. D.; Scudder, M. L. *Inorganic Chemistry* **1983**, *22*, 3785-3788.
(103) Pyykko, P. *Chemical Society Reviews* **2008**, *37*, 1967-1997.
(104) Schmidbaur, H.; Schier, A. *Chemical Society Reviews* **2008**, *37*, 1931-1951.
(105) Pyykko, P. *Chemical Reviews* **1997**, *97*, 597-636.
(106) Solodar, J.; Petrovich, J. P. *Inorganic Chemistry* **1971**, *10*, 395-397.
(107) Antonsen, O.; Benneche, T.; Undheim, K. *Acta Chemica Scandinavica Series B-Organic Chemistry and Biochemistry* **1988**, *42*, 515-523.
(108) Gauler, R.; Risch, N. *European Journal of Organic Chemistry* **1998**, 1193-1200.
(109) Beeston, R. F.; Aldridge, W. S.; Treadway, J. A.; Fitzgerald, M. C.; DeGraff, B. A.; Stitzel, S. E. *Inorganic Chemistry* **1998**, *37*, 4368-4379.
(110) Ye, Q.; Wang, X. S.; Zhao, H.; Xiong, R. G. *Chemical Society Reviews* **2005**, *34*, 208-225.
(111) Steel, P. J. *Accounts of Chemical Research* **2005**, *38*, 243-250.
(112) Lu, J. Y.; Schauss, V. *Inorganic Chemistry Communications* **2002**, *5*, 1028-1030.
(113) Lee, B.-W.; Twamley, B.; Shreeve, J. M. *Journal of Fluorine Chemistry* **2001**, *108*, 111-116.
(114) Yam, V. W. W.; Li, C. K.; Chan, C. L.; Cheung, K. K. *Inorganic Chemistry* **2001**, *40*, 7054-7058.
(115) Yam, V.; Chan, C.-L.; Choi, S.; Wong, M.-C.; Cheng, C.-C.; Yu, S.-C.; Ng, P.-K.; Chan, W.-K.; Cheung, K.-K. *Chemical Communications* **2000**, 53-54.
(116) O'Keefe, B. J.; Steel, P. J. *Crystal Engineering Communications* **2007**, *9*, 222-227.
(117) Pardo, E.; Carrasco, R.; Ruiz-Garcia, R.; Julve, M.; Lloret, F.; Munoz, M. C.; Journaux, Y.; Ruiz, E.; Cano, J. *Journal of the American Chemical Society* **2008**, *130*, 576-585.

(118) Zheng, X.-J.; Li, L.-C.; Gao, S.; Jin, L.-P. *Polyhedron* **2004**, *23*, 1257-1262.
(119) Mamula, O.; von Zelewsky, A.; Bark, T.; Bernardinelli, G. *Angewandte Chemie International Edition* **1999**, *38*, 2945-2948.
(120) Hartshorn, C. M.; Steel, P. J. *Inorganic Chemistry* **1996**, *35*, 6902-6903.
(121) Griffith, E. A. H.; Amma, E. L. *Journal of the American Chemical Society* **1974**, *96*, 743-749.
(122) Fukui, K.; Imamura, A.; Yonezawa, T.; Nagata, C. *Bulletin of the Chemical Society of Japan* **1961**, *34*, 1076-1080.
(123) Hall, E. A.; Amma, E. L. *Journal of the American Chemical Society* **1969**, *91*, 6538-6540.
(124) Gao, S.; Lu, Z.-Z.; Huo, L.-H.; Zhu, Z.-B.; Zhao, H. *Acta Crystallographica Section C-Crystal Structure Communications* **2005**, *61*, m22-m24.
(125) Cote, A. P.; Shimizu, G. K. H. *Inorganic Chemistry* **2004**, *43*, 6663-6673.
(126) Brunel, J. M. *Chemical Reviews* **2005**, *105*, 857-898.
(127) Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chemical Reviews* **2005**, *105*, 1801-1836.
(128) Telfer, S. G.; Kuroda, R. *Coordination Chemistry Reviews* **2003**, *242*, 33-46.
(129) Lee, S. J.; Lin, W. *Journal of the American Chemical Society* **2002**, *124*, 4554-4555.
(130) Lee, S. J.; Hu, A.; Lin, W. *Journal of the American Chemical Society* **2002**, *124*, 12948-12949.
(131) Lützen, A.; Hapke, M.; Griep-Raming, J.; Haase, D.; Saak, W. *Angewandte Chemie International Edition* **2002**, *41*, 2086-2089.
(132) Munakata, M.; Wu, L. P.; Sugimoto, K.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N.; Fujita, M. *Inorganic Chemistry* **1999**, *38*, 5674-5680.
(133) Mori, K.; Masuda, Y.; Kashino, S. *Acta Crystallographica Section C-Crystal Structure Communications* **1993**, *49*, 1224-1227.
(134) Poirier, M.; Simard, M.; Wuest, J. D. *Organometallics* **1996**, *15*, 1296-1300.
(135) Zefirov, Y. V.; Porai-Koshits, M. A. *Zhurnal strukturnoi khimii* **1980**, *21*, 150-155.
(136) Thalladi, V. R.; Weiss, H. C.; Blaser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *Journal of the American Chemical Society* **1998**, *120*, 8702-8710.
(137) Weiss, H. C.; Boese, R.; Smith, H. L.; Haley, M. M. *Chemical Communications* **1997**, 2403-2404.
(138) Prasanna, M. D.; Guru Row, T. N. *Crystal Engineering* **2000**, *3*, 135-154.
(139) Tominaga, M.; Suzuki, K.; Kawano, M.; Kusukawa, T.; Ozeki, T.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angewandte Chemie International Edition* **2004**, *43*, 5621-5625.
(140) Thebault, F.; Barnett, S. A.; Blake, A. J.; Wilson, C.; Champness, N. R.; Schroder, M. *Inorganic Chemistry* **2006**, *45*, 6179-6187.

(141) Marin, G.; Andruh, M.; Madalan, A. M.; Blake, A. J.; Wilson, C.; Champness, N. R.; Schrader, M. *Crystal Growth & Design* **2008**, *8*, 964-975.
(142) Clearfield, A.; Sharma, C. V. K.; Zhang, B. P. *Chemistry of Materials* **2001**, *13*, 3099-3112.
(143) Breslow, R.; Crispino, G. A. *Tetrahedron Letters* **1991**, *32*, 601-604.
(144) Han, Z.; Vaid, T. P.; Rheingold, A. L. *Journal of Organic Chemistry* **2008**, *73*, 445-450.
(145) Hu, S.; Chen, J.-C.; Tong, M.-L.; Wang, B.; Yan, Y.-X.; Batten, S. R. *Angewandte Chemie International Edition* **2005**, *44*, 5471-5475.
(146) Mueller, M. S.; Teich, F.; Puetter, H.; Schierle-Arndt, K.; Pastré, J.; *Journal of Material Chemistry* **2006**, *16*, 626 - 636.
(147) Olijnyk, V. V.; Goreshnik, E. A.; Davydov, V. N.; Mys'kiv, M. G. *Russian Journal of Coordination Chemistry* **1998**, *24*, 512 - 515.
(148) Olijnyk, V. V.; Aksel'rud, L. G. *Kristallografiya* **1994**, 1015.
(149) Olijnyk, V. V.; Zavalii, P. Y.; Mys'Kiv, M. G.; Fundamenskii, V. S. *Kristallografiya* **1986**, *31*, 284- 290.
(150) Olijnyk, V. V.; Filinchuk, Y. E.; Lenkivska, T. P. *Zeitschrift Fur Anorganische Und Allgemeine Chemie* **2008**, *634*, 1587-1590.
(151) Mykhalichko, B. M.; Olijnyk, V. V.; Mys'Kiv, M. G.; Zavalii, P. Y. *Koordinatsionnaya Khimiya* **1987**, *13*, 1536- 1540.
(152) Han, J.; Wu, H.; Zhi, S.; Li, Y.; Pan, Y. *Analytical Sciences X-ray Structure Analysis Online* **2006**, *22*, x299-x300.
(153) Krause, J.; Haack, K. J.; Cestaric, G.; Goddard, R.; Porschke, K. R. *Chemical Communications* **1998**, 1291-1292.
(154) Yamamoto, T.; Akimoto, M.; Yamamoto, A. *Chemistry Letters* **1983**, 1725-1726.
(155) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559-1567.
(156) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *Journal of the American Chemical Society* **1981**, *103*, 6863-6869.
(157) Goreshnik, E. A.; Schollmayer, D.; Olijnik, V. V. *Koordinatsionnaya Khimiya* **1997**, *23*, 773.
(158) Goreshnik, E. A.; Mys'kiv, M. G. *Koordinatsionnaya Khimiya* **1999**, *25*, 148.
(159) Olijnik, V. V.; Goreshnik, E. A.; Zhonchin'ska, Z.; Glowiak, T. *Koordinatsionnaya Khimiya* **1997**, *23*, 636.
(160) Filinchuk, Y. E.; Glowiak, T.; Mys'kiv, M. G. *Polish Journal of Chemistry* **1998**, *73*, 1283-1291
(161) Oliinik, V. V.; Mykhalichko, B. M.; Schollmeier, D.; Mys'kiv, M. G. *Russian Journal of Coordination Chemistry* **1997**, *23*, 352-355.
(162) Olijnyk, V.; Głowiak, T.; Mys'kiv, M. *Journal of Chemical Crystallography* **1995**, *25*, 621-624.
(163) Goreshnik, E. A.; Mys'kiv, M. G.; Simonov, Y. A.; Mazus, M. D.; Budarin, L. I. *Kristallografiya* **1992**, 100.

(164) Oliinik, V. V.; Mys'kiv, M. G.; Mazus, M. D.; Zavalii, P. Y.; Bon, P. S. *Journal of Structural Chemistry* **1992**, *33*, 103-107.
(165) Myskiv, M.; Goreshnik, E.; Pecharskii, V.; Oljinik, V. *Journal of Structural Chemistry* **1994**, *35*, 82-86.
(166) Vestergren, M.; Johansson, A.; Lennartson, A.; Håkansson, M. *Mendeleev Communications* **2004**, *14*, 258-260.
(167) Lindhorst, T. K.; Dubber, M.; Krallmann-Wenzel, U.; Ehlers, S. *European Journal of Organic Chemistry* **2000**, 2027-2034.
(168) Dong, Y.-B.; Geng, Y.; Ma, J.-P.; Huang, R.-Q. *Inorganic Chemistry* **2005**, *44*, 1693-1703.
(169) Dong, Y.-B.; Geng, Y.; Ma, J.-P.; Huang, R.-Q. *Organometallics* **2006**, *25*, 447-462.
(170) Baier, M.; Gleiter, R.; Rominger, F. *European Journal of Organic Chemistry* **2006**, *2006*, 5264-5278.
(171) Richards, P. I.; Bickley, J. F.; Boomishankar, R.; Steiner, A. *Chemical Communications* **2008**, 1656-1658.
(172) Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; White, A. H. *Australian Journal of Chemistry* **1989**, *42*, 185-199.
(173) Wang, X.-S.; Zhao, H.; Li, Y.-H.; Xiong, R.-G.; You, X.-Z. *Topics in Catalysis* **2005**, *35*, 43-61.
(174) Xie, Y.-R.; Wang, X.-S.; Zhao, H.; Zhang, J.; Weng, L.-H.; Duan, C.-Y.; Xiong, R.-G.; You, X.-Z.; Xue, Z.-L. *Organometallics* **2003**, *22*, 4396-4398.
(175) Qu, Z.-R.; Chen, Z.-F.; Zhang, J.; Xiong, R.-G.; Abrahams, B. F.; Xue, Z.-L. *Organometallics* **2003**, *22*, 2814-2816.
(176) Almeida Paz, F. A.; Shi, F.-N.; Klinowski, J.; Rocha, J.; Trindade, T. *European Journal of Inorganic Chemistry* **2004**, *2004*, 2759-2768.
(177) Feng, W.; Xu, Y.; Zhou, G.; Zhang, C.; Zheng, X. *Inorganic Chemistry Communications* **2007**, *10*, 49-52.
(178) Chen, B.; Fronczek, F. R.; Maverick, A. W. *Inorganic Chemistry* **2004**, *43*, 8209-8211.
(179) Westwell, A. D.; Williams, J. M. J. *Tetrahedron* **1997**, *53*, 13063-13078.
(180) Hannon, M. J.; Childs, L. J. *Supramolecular Chemistry* **2004**, *16*, 7 - 22.
(181) Cook, B. W.; Miller, R. G. J.; Todd, P. F. *Journal of Organometallic Chemistry* **1969**, *19*, 421-430.
(182) Springborg, J.; Schaffer, C. E. *Acta chemica Scandinavica. Series A-Physical and Inorganic Chemistry* **1973**, *27*, 3312 - 3322.
(183) Wang, X. S.; Zhao, H.; Li, Y. H.; Xiong, R. G.; You, X. Z. *Topics in Catalysis* **2005**, *35*, 43-61.
(184) Lebigot, Y.; Delmas, M.; Gaset, A. *Tetrahedron Letters* **1983**, *24*, 193-196.
(185) Echavarren, A. M.; Stille, J. K. *Journal of the American Chemical Society* **1988**, *110*, 1557-1565.
(186) Steiger, D.; Weder, C.; Smith, P. *Macromolecules* **1999**, *32*, 5391-5398.
(187) Gates, B. D.; Dalidowicz, P.; Tebben, A.; Wang, S. P.; Swenton, J. S. *Journal of Organic Chemistry* **1992**, *57*, 2135-2143.

(188) Ranu, B. C.; Dutta, J.; Guchhait, S. K. *Journal of Organic Chemistry* **2001**, *66*, 5624-5626.
(189) Carreno, M. C.; Hernandez-Sanchez, R.; Mahugo, J.; Urbano, A. *Journal of Organic Chemistry* **1999**, *64*, 1387-1390.
(190) Schrievers, T.; Brinker, U. H. *Synthesis-Stuttgart* **1988**, 330-331.
(191) Bruhn, J.; Zsindely, J.; Schmid, H.; Fráter, G. *Helvetica Chimica Acta* **1978**, *61*, 2542-2559.
(192) Mariano, P. S.; Krochmal, E.; Beamer, R.; Huesmann, P. L.; Dunawaymariano, D. *Tetrahedron* **1978**, *34*, 2609-2616.